



# Prediction of the rovibrational emission spectroscopy of $B^2\Sigma^+ - X^2\Sigma^+$ system in $^{12}C^{17}O^+$

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## ABSTRACT

An analytical formula based on the Herzberg's conventional rovibrational energy levels for diatomic system is proposed by taking multiple differences of spectral lines to predict the R-branch high-lying rovibrational emission spectroscopy, where only 15 accurate known transition lines and rotational constants  $D_{v'}$ ,  $D_{v''}$  are needed. Using the formula, the  $R_{11ee}$  and  $R_{22ff}$  branches of (0, 2) and (0, 3) transition bands in the  $B^2\Sigma^+ - X^2\Sigma^+$  system of  $^{12}C^{17}O^+$  are studied. The results show that not only the relatively lower order rovibrational transition lines given by experiments are reproduced but also the higher and the absent spectral lines are correctly predicted for each band.

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## 1. Introduction

Extensive studies have been performed to investigate the emission spectral lines or the rovibrational energy levels of diatomic systems [1–6]. Many techniques, such as the Fourier's transform spectrometer (FTS) [7,8], the laser induced fluorescence (LIF) [9], the optical heterodyne magnetic rotation enhanced velocity modulation spectroscopy (OH-MR-VMS) [10], and the intracavity laser absorption spectroscopy (ILS) [11,12], etc. have been used to investigate the rovibrational transition spectra of some diatomic molecules or diatomic ions. Most of these experimental approaches can obtain some low-lying transition lines for a given vibrational transition band from  $v'$  to  $v''$ . For the high-lying ones it is difficult to observe as a result of the limitation of the resolution of the equipments.

On the other hand, many theoretical studies such as quantum mechanical calculations [13,14], variational–numerical approach [15], Dunham method [16] and so on have also been carried out on the rovibrational spectroscopy of diatomic systems. However, due to the reasons described in ref. [17,18], it is also difficult to give high-lying transition lines theoretically for many vibrational transition bands.

In our recent study, an analytical formula has been developed to accurately predict the unknown P-branch high-lying

rovibrational transition lines based on a set of known low-lying experimental transition data [17]. The present study is one of the series works which predict high-lying rovibrational transition lines for different branches of diatomic systems, and proposes an analytical formula for R-branch spectrum by taking multiple spectral differences of the Herzberg's general energy expression for vibrational–rotational diatomics. Section 2 presents the new formula and the method. Section 3 applies the formula to predict the R-branch transitional spectral lines for the (0, 2) and (0, 3) bands of the  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  system of  $^{12}C^{17}O^+$  which has been extensively studied by astronomers and spectroscopy scientists [19–21]. Section 4 summarizes this study. The derivation of the new formula is given in the [Supplemental Information](#).

## 2. Theory and method

The following formula is the equation (A21) in (the [supplementary information](#)), and can be utilized to predict the R-branch transition spectral lines of diatomic system,

$$\begin{aligned} \nu_{J_{16}} = & (\nu_{J_{15}} + \nu_{J_{14}} - \nu_{J_{13}}) + (\nu_{J_{12}} - \nu_{J_{11}} - \nu_{J_{10}} + \nu_{J_9}) \frac{S_5}{S_6} \\ & + (\nu_{J_8} - \nu_{J_7} - \nu_{J_6} + \nu_{J_5}) \frac{S_2}{S_6} - (\nu_{J_4} - \nu_{J_3} - \nu_{J_2} + \nu_{J_1}) \frac{S_1}{S_6} \\ & + D_{v'} \left( \frac{S_7}{S_6} - \frac{S_3}{S_6} \right) - D_{v''} \left( \frac{S_8}{S_6} - \frac{S_4}{S_6} \right) \end{aligned} \quad (1)$$

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In this formula ( $\nu_{J_1}, \nu_{J_2}, \dots, \nu_{J_{15}}$ ) are the transition spectral lines selected from a group of known experimental R-branch transition lines for a given ( $\nu', \nu''$ ) transition band of a diatomic system, and ( $J_1, J_2, \dots, J_{15}$ ) are the corresponding rotational quantum numbers, respectively. In Eq. (1),  $D_{\nu'}$  and  $D_{\nu''}$  are the centrifugal distortion constants for the vibrational states  $\nu'$  and  $\nu''$ , respectively, ( $S_1, S_2, S_3, S_4$ ) are (through the  $a_k$  functions) the functions of rotational quantum numbers ( $J_1, J_2, \dots, J_8$ ), and ( $S_5, S_6, S_7, S_8$ ) are those of ( $J_9, J_{10}, \dots, J_{16}$ ) as defined in equations (A12)–(A15) and equations (A17)–(A20), respectively in **Supplementary Information**. Obviously, from the formulism of Eq. (1) it is noticed that when 15 known experimental transition lines ( $\nu_{J_1}, \dots, \nu_{J_{15}}$ ) and the centrifugal distortion constants ( $D_{\nu'}, D_{\nu''}$ ) are given accurately, one can predict the correct value of the unknown transition line  $\nu_{J_{16}}$  of a R-branch or a sub-R-branch of a transition band ( $\nu', \nu''$ ) for a given rotational state  $J_{16}$  of a diatomic system. When deriving the formula there is no particular limitation on the rotational quantum states enforced as long as the functions  $a_k \neq 0$  and  $S_n \neq 0$  that are defined by rotational states  $J$ 's. Therefore, some of the rotational quantum states may be used more than once when equation (1) is used to evaluate correct transition spectral values.

It is not easy for experimental studies to get the high-lying rovibrational transition lines for a given band ( $\nu', \nu''$ ) of two electronic states due to limitations of experimental facilities. However, for a given transition band ( $\nu', \nu''$ ), a subgroup of accurate transition lines [ $\nu_{J'}$ ] with relatively lower rotational quantum number  $J$ 's can almost always be observed, and the centrifugal distortion constants ( $D_{\nu'}, D_{\nu''}$ ) corresponding to the relevant vibrational states can also be obtained accurately. Then Eq. (1) and the following protocol can be used to predict the correct value of any spectral line  $\nu_J$  that has not been observed experimentally:

- Choose 15 transition lines at a time from the  $m$  known accurate experimental transition data for rotational states ( $J_1, J_2, \dots, J_m$ ) of a given vibrational transition band ( $\nu', \nu''$ ). There will be  $N = C_m^{15}$  such selections.
- Calculate ( $m+k$ ) transition lines [ $\nu_{J_1}, \dots, \nu_{J_m}; \nu_{J_{m+1}}, \dots, \nu_{J_{m+k}}$ ] $_{i,cal}$  using Eq. (1) and the 15 selected spectral lines in the set  $i$  of the  $N$  sets of data. One may get  $N$  sets of such evaluated spectral lines for  $i = 1, 2, \dots, N$ . Not only the  $m$  known data [ $\nu_{J_1}, \nu_{J_2}, \dots, \nu_{J_m}$ ] $_{i,cal}$  are correctly reproduced, but also the reliable values of the unknown spectral lines [ $\nu_{J_{m+1}}, \nu_{J_{m+2}}, \dots, \nu_{J_{m+k}}$ ] $_{i,cal}$  for  $k$  rotational states ( $J_{m+1}, J_{m+2}, \dots, J_{m+k}$ ) are given in each set.
- The 15 experimental transition data in a set (say set  $n$ ) that best (compared with other  $N-1$  sets) represent the embedded physics of all  $m$  known spectral lines are found if the theoretical spectral lines evaluated from the 15 data in set  $n$  best satisfy the following physical requirements:

$$\frac{1}{m} \sum_{J_1}^{J_m} |\nu_{J, \text{expt}} - \nu_{J, \text{cal}}| \rightarrow 0 \quad (2)$$

$$\frac{1}{m} \sum_{J_1}^{J_m} |\Delta_{J, \text{expt}} - \Delta_{J, \text{cal}}| \rightarrow 0 \quad \Delta_J = \nu_J - \nu_{J-1} \quad (3)$$

$$\frac{1}{m} \sum_{J_1}^{J_m} \{ |\Delta_{J, \text{expt}} / \nu_{J, \text{expt}}| - |\Delta_{J, \text{cal}} / \nu_{J, \text{cal}}| \} \rightarrow 0 \quad (4)$$

where  $\Delta_J$  is the spectral difference. Therefore, the best physical representation of the unknown spectral lines [ $\nu_{J_{m+1}}, \dots, \nu_{J_{m+k}}$ ] $_{\text{best}}$  are generated this way using Eq. (1).

Since there are no physical approximations or mathematical models used in deriving equation (1), and the only approximation

is that all the high order terms with absolute values of the rotational constants of the order of  $10^{-10} \text{ cm}^{-1}$  and smaller in the rotational energy expansion are neglected, one can calculate any unknown rovibrational transition line using Eq. (1), 15 accurate spectral lines and two centrifugal distortion constants ( $D_{\nu'}, D_{\nu''}$ ) obtained from experimental study. As long as the 15 selected experimental transition lines are accurate enough, one can obtain the accurate unknown spectral lines using the new formula that combines the advantage of modern experimental technology and the merit of the correct theoretical method.

### 3. Application and discussion

The R-branch emission spectral lines of the (0,2) and (0,3) bands of the  $B^2\Sigma^+ - X^2\Sigma^+$  system of  $^{12}\text{C}^{17}\text{O}^+$  molecular ion are studied using the new formula and the protocol presented above. In this case, the transition lines of each band split into two branches  $\{R_{11ee}$  and  $R_{22ff}\}$  with small differences between each other. In Table 1, the centrifugal distortion constants  $D_{\nu}$  of each vibrational state  $\nu$ , and the rotational quantum numbers ( $J_1, \dots, J_{15}$ ) of the selected experimental spectral lines used in the final calculation are listed. It is noticed that some of the rotational states are used more than once as long as the functions  $a_i$  and  $S_n$  defined by these states are not zero. This says that although Eq. (1) theoretically needs 15 known transition lines to predict an unknown line, it may actually use fewer than 15. Table 2 (see the supplementary information) lists all the R-branch experimental transition lines  $\nu_{J, \text{expt}}$  for each of the bands studied, the spectral lines  $\nu_{J, \text{cal}}$  up to  $J_{\text{max}}^{\text{cal}} = 65.5$  calculated using Eq. (1), the spectral difference (expt. – cal.) between experimental and theoretical data, the experimental spectral difference  $\Delta_{J, \text{expt}} (= \nu_J - \nu_{J-1})_{\text{expt}}$ , the calculated spectral difference  $\Delta_{J, \text{cal}}$ , the experimental spectral ratio  $\text{Ratio}_{J, \text{expt}}$  and the calculated spectral ratio  $\text{Ratio}_{J, \text{cal}}$ , respectively. For each band, the selected 15 experimental emission spectral lines are marked in bold face, and the corresponding rotational quantum numbers can be found in Table 1, respectively. All quantities but the ratio are in  $\text{cm}^{-1}$ . It can be seen that the spectral lines predicted with Eq. (1) for each band meet the physical requirements of Eqs. (2)–(4). It is shown that the spectral lines evaluated with Eq. (1) not only reproduce the given experimental data, but also predict the correct values of

**Table 1**

Rotational constants and rotational quantum numbers  $J$ 's of the 15 selected known experimental spectral lines of the R-branch (0, 2) and (0, 3) bands of the  $B^2\Sigma^+ - X^2\Sigma^+$  transition in the  $^{12}\text{C}^{17}\text{O}^+$  molecular ion.

| $B^2\Sigma^+$ | $\nu$      | $D_{\nu} \times 10^6 (\text{cm}^{-1})$ |                    |
|---------------|------------|--|--------------------|
|               |            | 0                                      | 2                  |
| $X^2\Sigma^+$ | 2          | 7.584 <sup>a</sup>                     | 6.059 <sup>a</sup> |
|               | 3          | 6.037 <sup>a</sup>                     | 6.037 <sup>a</sup> |
| (0, 2) Band   |            |  |                    |
|               | $P_{11ee}$ | $P_{22ff}$                             |                    |
| $J_1$         | 2.5        | 27.5                                   | 3.5                |
| $J_2$         | 2.5        | 18.5                                   | 32.5               |
| $J_3$         | 23.5       | 18.5                                   | 4.5                |
| $J_4$         | 2.5        | 3.5                                    | 18.5               |
| $J_5$         | 8.5        | 3.5                                    | 8.5                |
| $J_6$         | 4.5        | 15.5                                   | 10.5               |
| $J_7$         | 20.5       | 1.5                                    | 13.5               |
| $J_8$         | 28.5       | 19.5                                   | 10.5               |
| $J_9$         | 28.5       | 23.5                                   | 22.5               |
| $J_{10}$      | 21.5       | 4.5                                    | 6.5                |
| $J_{11}$      | 9.5        | 23.5                                   | 7.5                |
| $J_{12}$      | 25.5       | 24.5                                   | 25.5               |
| $J_{13}$      | 26.5       | 27.5                                   | 5.5                |
| $J_{14}$      | 20.5       | 30.5                                   | 28.5               |
| $J_{15}$      | 3.5        | 2.5                                    | 33.5               |
| (0, 3) Band   |            |  |                    |
|               | $P_{11ee}$ | $P_{22ff}$                             |                    |
| $J_1$         | 2.5        | 27.5                                   | 3.5                |
| $J_2$         | 2.5        | 18.5                                   | 32.5               |
| $J_3$         | 23.5       | 18.5                                   | 4.5                |
| $J_4$         | 2.5        | 3.5                                    | 18.5               |
| $J_5$         | 8.5        | 3.5                                    | 8.5                |
| $J_6$         | 4.5        | 15.5                                   | 10.5               |
| $J_7$         | 20.5       | 1.5                                    | 13.5               |
| $J_8$         | 28.5       | 19.5                                   | 10.5               |
| $J_9$         | 28.5       | 23.5                                   | 22.5               |
| $J_{10}$      | 21.5       | 4.5                                    | 6.5                |
| $J_{11}$      | 9.5        | 23.5                                   | 7.5                |
| $J_{12}$      | 25.5       | 24.5                                   | 25.5               |
| $J_{13}$      | 26.5       | 27.5                                   | 5.5                |
| $J_{14}$      | 20.5       | 30.5                                   | 28.5               |
| $J_{15}$      | 3.5        | 2.5                                    | 33.5               |

<sup>a</sup> The rotational constants given in Ref. [21].

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