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# Simultaneous Analysis of the Ballik-Ramsay and Phillips Systems of C2 and Observation of Forbidden Transitions Between Singlet and Triplet **States**

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# Simultaneous analysis of the Ballik-Ramsay and Phillips systems of C<sub>2</sub> and **observation of forbidden transitions between singlet and triplet states**

[Wang Chen,](http://aip.scitation.org/author/Chen%2C+Wang) [Kentarou Kawaguchi](http://aip.scitation.org/author/Kawaguchi%2C+Kentarou), [Peter F. Bernath](http://aip.scitation.org/author/Bernath%2C+Peter+F), and [Jian Tang](http://aip.scitation.org/author/Tang%2C+Jian)

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## **[Simultaneous analysis of the Ballik-Ramsay and Phillips systems of C](http://dx.doi.org/10.1063/1.4907530)<sup>2</sup> [and observation of forbidden transitions between singlet and triplet states](http://dx.doi.org/10.1063/1.4907530)**

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6229 lines of the Ballik-Ramsay system  $(b^3\Sigma_g^2 - a^3\Pi_u)$  and the Phillips system  $(A^1\Pi_u - X^1\Sigma_g^+)$  of  $C_2$  up to  $v = 8$  and  $J = 76$ , which were taken from the literature or assigned in the present work, were analyzed simultaneously by least-squares fitting with 82 Dunham-like molecular parameters and spin-orbit interaction constants between the  $b^3\Sigma_g^-$  and  $X^1\Sigma_g^+$  states with a standard deviation<br>of 0.0027 cm<sup>-1</sup> for the whole data ast. As a result of the departurbation englysis, the grip orbit of 0.0037 cm<sup>-1</sup> for the whole data set. As a result of the deperturbation analysis, the spin-orbit interaction constant  $A_{bX}$  was determined as 6.333(7) cm<sup>-1</sup> and the energy difference between the  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  states was determined as 720.008(2) cm<sup>-1</sup> for the potential minima or 613.650(3) cm−<sup>1</sup> for the v = 0 levels with Merer and Brown's *N* <sup>2</sup> Hamiltonian for <sup>3</sup>Π states, which is about 3.3 cm<sup>−</sup><sup>1</sup> larger than the previously determined value. Due to this sizable change, a new energy-level crossing was found at *J* = 2 for v = 3 (F<sub>1</sub>) of  $b^3\Sigma_g^-$  state and v = 6 of  $X^1\Sigma_g^+$  state, where the strong<br>interaction square a possible complete mixing of the way functions of the  $b^3\Sigma_0^-$  and  $X^1\Sigma_0^+$  states interaction causes a nearly complete mixing of the wave functions of the  $b^3\Sigma_g^-$  and  $X^1\Sigma_g^+$  states and the forbidden transitions because observable. Heing the prodictions of our departments applicition in a state of the forbidden transitions become observable. Using the predictions of our deperturbation analysis, we were able to identify 16 forbidden transitions between the singlet and triplet states at the predicted frequencies with the expected intensities, which verifies our value for the energy difference between the  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  states. © 2015 AIP Publishing LLC. [\[http:](http://dx.doi.org/10.1063/1.4907530)//[dx.doi.org](http://dx.doi.org/10.1063/1.4907530)/[10.1063](http://dx.doi.org/10.1063/1.4907530)/[1.4907530\]](http://dx.doi.org/10.1063/1.4907530)

### **I. INTRODUCTION**

 $C_2$  is ubiquitous in astronomical environments, flames, and carbon plasmas used to make nanostructures.<sup>[1](#page-11-0)</sup> Due to the presence of many low-lying electronic states in  $C_2$ , various vibronic band systems, such as the Swan system  $(d^{3}\Pi_{g}-a^{3}\Pi_{u})$ ,<br>the Phillips system  $(d^{1}\Pi_{g}-V^{1}\Sigma_{g}^{+})$ , and the Pallila Bemsex: the Phillips system  $(A^{1}\Pi_{u}-X^{1}\Sigma_{g}^{+})$ , and the Ballik-Ramsay<br>system  $(B^{3}\Sigma - s^{3}\Pi_{g})$ , house heave absented in the visible and system  $(b^3\Sigma_g - a^3\Pi_u)$ , have been observed in the visible and<br>infrared regions and studied automaiusly for a lang time <sup>2</sup> infrared regions and studied extensively for a long time.<sup>[2](#page-11-1)</sup>

The congestion of the vibronic states in  $C_2$ , as shown in Fig. [1,](#page-3-0) often causes perturbations in the observed spectra due to interactions between the accidentally crossing rotational levels. These perturbations provide information on the energy difference between electronic states with different multiplicities and sometimes even locate unknown or dark electronic states. Historically, the perturbations observed for the Phillips system and the Ballik-Ramsay system were found to be due to the spin-orbit interaction between the  $X^1\Sigma_g^+$  and  $h^3\Sigma =$  states  $\frac{3}{2}$  and a denote the conduction and the spin-orbit  $b^3\Sigma_g$  $b^3\Sigma_g$  $b^3\Sigma_g$ <sup>-</sup> states,<sup>3</sup> and a deperturbation analysis located the  $a^3\Pi_u$ state 610 ± 5 cm<sup>-1</sup> above the  $X^1\Sigma_g^+$  ground state for the v = 0 vibrational energy levels,<sup>[4](#page-11-3)</sup> or  $716.24 \pm 5$  cm<sup>-1</sup> for the potential minima of the two electronic states <sup>5</sup>. The small potential minima of the two electronic states.<sup>[5](#page-11-4)</sup> The small perturbations observed in the upper  $A<sup>1</sup>\Pi_u$  state of the Phillips system also led to the prediction of a dark  $c^3 \Sigma_u^+$  state.<sup>[5–](#page-11-4)[7](#page-11-5)</sup> Finally, in 2006, Kokkin *et al.*[8](#page-11-6) successfully observed the new  $d^3\Pi_g - c^3\Sigma_u^+$  system by laser-induced fluorescence (LIF)

spectroscopy.<sup>[9](#page-11-7)</sup> Interestingly, Nakajima and Endo<sup>[10](#page-11-8)</sup> carried out a recent deperturbation analysis for the  $c^3\Sigma_u^+$ ,  $a^3\Pi_u$ , and  $A^1\Pi_u$ states for their observed LIF spectrum of the  $d^3\Pi_g - c^3\Sigma_u^+$ system and the Swan system, which indicated that there are no significant level shifts caused by the spin-orbit interaction between  $v = 2$  of  $A^1\Pi_u$  and  $v = 1(F_2)$  of  $c^3\Sigma_u^+$ . The small perturbations observed previously for  $J = 19$  and 21 of  $A<sup>1</sup>\Pi_u$  $(v = 2)$  of the Phillips system, which led to the well-known prediction of the  $c^3\Sigma_u^+$  dark state, are in fact due to the interaction between  $v = 2$  of  $A<sup>1</sup>\Pi_u$  and  $v = 7(F_2)$  of  $a<sup>3</sup>\Pi_u$ . As another example, many perturbations for the upper  $d^3\Pi_g$  state of the Support with two states were ethnical to vibronic interactions with two Swan system were attributed to vibronic interactions with two unknown  $B^1\Delta_g$  and  $B'^1\Sigma_g^+$  states and high vibrational levels of<br>the  $b^3\Sigma$  = and  $V^1\Sigma$  + states 11 Later in 1988. Bernath and so the  $b^3\Sigma_g$ <sup>-</sup> and  $X^1\Sigma_g$ <sup>+</sup> states.<sup>[11](#page-11-9)</sup> Later in 1988, Bernath and co-<br>workers observed the PlA 4<sup>1</sup>H and P<sup>1</sup>N <sup>+</sup> 4<sup>1</sup>H systems workers observed the  $B^1\Delta_g - A^1\Pi_u$  and  $B'^1\Sigma_g^+ - A^1\Pi_u$  systems in the infrared region.<sup>[12](#page-11-10)</sup> The abnormal intensity enhancement observed in the Swan system for the  $d^3\Pi_g$ , v = 6 vibrational<br>layel (the see salled high greenure hands) was greeneed to be level (the so called high pressure bands) was proposed to be caused by the perturbation of an unknown  $1^5\Pi_g$  dark state.<sup>[13](#page-11-11)</sup> In 2011, Bornhauser *et al.*[14](#page-11-12) observed the forbidden transitions between the  $I^5\Pi_g$  and  $a^3\Pi_u$  states due to the vibronic mixing<br>of  $d^3\Pi_u$  and  $I^5\Pi_v$  by double resonance four wave mixing of  $d^3\Pi_g$  and  $I^5\Pi_g$  by double-resonance four-wave mixing<br>spectroscopy and acquirately determined the energy difference spectroscopy and accurately determined the energy difference between the  $I^{5}\Pi_{g}$  and  $a^{3}\Pi_{u}$  states as 29 258.592(5) cm<sup>-1</sup>. In contrast, the energy difference between the  $a^3\Pi_u$  and  $X^1\Sigma_g^+$ states has not been determined directly by observing forbidden transitions between the singlet and triplet states of  $C_2$ .

The initial deperturbation analysis by Ballik and Ramsay<sup>[3–](#page-11-2)[5](#page-11-4)</sup> for the interaction between the  $X^1\Sigma_g^+$  and  $b^3\Sigma_g^-$ 

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<span id="page-3-0"></span>

 $c^3 \Sigma_u^+$ 24704

 $\frac{22850}{7}$ 

 $\frac{17228}{4}$ 

15284

 $\frac{13311}{2}$ 

11309

 $\frac{9277}{0}$ 

FIG. 1. Vibronic energy levels of  $C_2$ below 25 000 cm−<sup>1</sup> . The levels which have been observed so far are drawn with bold lines. The values below the levels are the vibrational quantum numbers, and the upper values are term energies  $T_v$  in cm<sup>-1</sup> relative to the vibrational level  $v = 0$  of  $X^{1}\Sigma_{g}^{+}$ ,<br>which are from Bef 10 ( $V^{1}\Sigma_{g}^{+}$  and which are from Ref. [19](#page-11-13)  $(X^{1}\Sigma_{g}^{+}$  and<br> $A^{1}\Pi$ ) Pef. 28  $(a^{3}\Pi)$  and  $A^{3}\Pi$ )  $A^1\Pi_u$ ), Ref. [28](#page-11-14)  $(a^3\Pi_u$  and  $d^3\Pi_g$ ),<br>Bef. 15  $(b^3\Sigma)^{-1}$ , Bef. 12  $(B^1\Lambda)$  and Ref. [15](#page-11-15) ( $b^3\Sigma_g^-$ ), Ref. [12](#page-11-10) ( $B^1\Delta_g$  and  $B'^{1}\Sigma_{g}^{+}$ ), and Ref. [29](#page-11-16) ( $c^{3}\Sigma_{u}^{+}$  and many higher v states of the other electronic states). The singlet-triplet gap between v = 0 of  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  is taken<br>as 613.650(3) cm<sup>-1</sup> from the present as  $613.650(3)$  cm<sup>-1</sup> from the present study. The dashed lines between the levels indicate that perturbations near the level crossing have been observed, and the values within the brackets are the J-values at the level crossings. The level crossing at  $J = 2$  of  $b^3\Sigma_g^2$  v = 3<br>(E) and  $X^1\Sigma + y = 6$  was found in the (F<sub>1</sub>) and  $X^1\Sigma_g^+$  v = 6 was found in the present study.

states was carried out for 9 emission bands of the Ballik-Ramsay system involving levels of the  $b^3\Sigma_g^-$  state up to  $\cdots$  - 4 which were changed by a year infrared grating  $v = 4$ , which were observed by a vacuum infrared grating spectrometer with a spectral resolution of  $0.01$ - $0.05$  cm<sup>-1</sup> and absolute accuracy of around 0.05 cm<sup>−</sup><sup>1</sup> . Later, Amiot *et al.*[15](#page-11-15) observed 14 emission bands of the Ballik-Ramsay system involving levels of the  $b^3\Sigma_g^-$  state up to  $v = 7$  with a Fourier<br>transform infrared (ETIB) apartmeter with a resolution of transform infrared (FTIR) spectrometer with a resolution of 0.028 cm<sup>−</sup><sup>1</sup> , and their deperturbation analysis resulted in an energy difference of  $\Delta E$  ( $a^3 \Pi_u - X^1 \Sigma_g^+$ ) = 718.32 cm<sup>-1</sup> in<br>comparison with the requirements of 716.24 cm<sup>-1</sup>. Bows comparison with the previous value of 716.24 cm<sup>−</sup><sup>1</sup> . Roux *et al.*[16](#page-11-17) then carried out a new FTIR measurement with a resolution of 0.013 cm<sup>−</sup><sup>1</sup> and corrected many errors in the previous assignment<sup>[15](#page-11-15)</sup> of the Ballik-Ramsay system near the perturbation. As a result, the deperturbation analysis for the spin-orbit interaction constants between the  $X^1\Sigma_g^+$  and  $b^3\Sigma_g^-$ <br>states was improved by the inclusion of a higher order term <sup>16</sup> states was improved by the inclusion of a higher-order term.<sup>[16](#page-11-17)</sup> In all these previous analyses, effective molecular constants for each vibrational level were determined first with the

"unperturbed" transitions of the Ballik-Ramsay system, and the deperturbation was carried out by analyzing the shifts of the "perturbed" transition frequencies from the values calculated with the effective molecular constants obtained from the "unperturbed" transitions. Then, a Dunham-like vibrational expansion of the molecular constants was obtained by analysis of the effective molecular constants for the various vibrational levels, and the energy difference and the spin-orbit interaction constants between the  $X^1\Sigma_g^+$  and  $b^3\Sigma_g^-$  states were derived by a deperturbation analysis. These analyses have omitted the vibronic interaction for the "unperturbed" transitions near the "perturbed" transitions, which means that the effective molecular constants for the "unperturbed" transitions are, in fact, affected partly by the backgroundlike vibronic interactions. In addition, the derived energy difference and the spin-orbit interaction constants are also affected by the incomplete shift of the "perturbed" transition frequencies. In other words, these previous analyses are only a partial deperturbation.

In the analysis of the pure rotational transitions of MgO within the  $X^1\Sigma$  and  $a^3\Pi$  states, <sup>[17](#page-11-18)</sup> a simultaneous deperturbation for all the transitions involving the  $X^1\Sigma$ ,  $a^3\Pi$ , and  $A^1\Pi$ states was successful by fitting a set of molecular constants with vibrational expansions, the spin-orbit interaction between  $X$ <sup>1</sup>Σ and  $a$ <sup>3</sup>Π, and the orbit-rotation interaction between  $X$ <sup>1</sup>Σ and  $A<sup>1</sup>\Pi$  and by using calculated vibrational overlap integrals and  $\langle v_A|B(r)|v_X\rangle$ . In a similar analysis, in the present study, we analyzed all the transitions ("perturbed" and "unperturbed") simultaneously for the Phillips system and the Ballik-Ramsay system of  $C_2$  directly using Dunham-like molecular constants with vibrational expansions. The more complete deperturbation for  $C_2$  resulted in a new energy difference of  $\Delta E$  ( $a^3 \Pi_u - X^1 \Sigma_g$ <sup>+</sup>) = 721.640 (2) cm<sup>-1</sup>, a change of 3.3 cm<sup>-1</sup> from the previous value, which led to the discovery of a new level-crossing with a very strong perturbation. Eventually, the forbidden transitions between the singlet and triplet electronic states were found at this level crossing, which in turn confirmed our new value of the singlet-triplet energy difference.

### <span id="page-4-7"></span>**II. DATA SET FOR ANALYSIS**

The data used for the present analysis, about 6229 lines (16 lines due to forbidden transitions are included), were partly taken from previous studies and partly assigned in this work, as summarized in Table [I.](#page-4-0) For the 4878 transitions of the Ballik-Ramsay system, we took 1294 lines from the FTIR spectrum of Roux *et al*.<sup>[16](#page-11-17)</sup> with a spectral resolution of 0.013 cm<sup>-1</sup>, 527 lines from the FTIR spectrum of Amiot *et al.*[15](#page-11-15) with a spectral resolution of 0.028 cm<sup>−</sup><sup>1</sup> , and 112 lines of satellite branches for the  $v'$ - $v''$  = 0-0 band of the Ballik-Ramsay system with interconnections between the different *F* levels from the FTIR spectrum of Davis *et al.*<sup>[18](#page-11-19)</sup> with a spectral resolution of  $0.015 \text{ cm}^{-1}$ . For the 1335 transitions of the Phillips system, we took 500 lines from the FTIR spectrum of Douay *et al.*[19](#page-11-13) with a spectral resolution of 0.013 cm<sup>−</sup><sup>1</sup> , 283 lines from the laser absorption

<span id="page-4-0"></span>TABLE I.  $C_2$  bands used in the present analysis.

spectrum of Chan *et al.*<sup>[20](#page-11-20)</sup> with a spectral resolution of 0.013 cm−<sup>1</sup> , and 145 lines from the FTIR spectrum of Chauville *et al.*[6](#page-11-21) with a spectral resolution of 0.026-0.040  $cm^{-1}$ . In the present work, we assigned the rest of 3368 lines for 11 bands of the Phillips system and 12 bands of the Ballik-Ramsay system, as shown in Table [I,](#page-4-0) and the satellite branches for the  $v'-v'' = 1-0$ , 2-1, 3-2, 0-1, 1-2, 2-3, and 3-4 bands of the Ballik-Ramsay system with interconnections between the different *F* levels from the FTIR spectrum of Ghosh *et al.*[21](#page-11-22) with a spectral resolution of 0.02 cm<sup>-1</sup> and from the FTIR spectrum of Douay *et al.*<sup>[19](#page-11-13)</sup> Previously, Yan *et al.* observed the v'-v'' = 0-1, 1-2, 2-3 bands of the Ballik-Ramsay system by laser spectroscopy with magnetic rotation.<sup>[22](#page-11-23)</sup> The bands associated with  $v = 4$  of *a* <sup>3</sup>Π are mostly assigned in our present analysis. The complete line list used is available online as supplementary material.<sup>[23](#page-11-24)</sup> We have also assigned several bands associated with  $v = 5$ and 6 of  $a^3\Pi$  as shown in the supplementary material, but they were not included in the present deperturbation analysis due to some new perturbations other than the ones considered in this work, which may be caused by the interactions with the  $c^3\Sigma_u^+$ state. The deperturbation analysis is still under way for a future publication.

#### **III. DEPERTURBATION ANALYSIS**

The standard energy level expressions for the  $X^1\Sigma_g^+$  and  $A$ <sup>1</sup> $\Pi$ <sub>u</sub> states are

$$
E(X^{1}\Sigma_{g}^{+}) = G_{v} + B_{v}x - D_{v}x^{2},
$$
  
\n
$$
E(A^{1}\Pi_{u}) = T_{e} + G_{v} + B_{v}(x - 1) - D_{v}(x - 1)^{2}
$$
  
\n
$$
\pm \frac{1}{2}(q_{v}x + q_{D}x^{2}),
$$

in which  $T_e$  is the electronic energy,  $x = J(J + 1)$ , and

$$
G_{v} = \omega_{e} (v + \frac{1}{2}) - \omega_{e} x_{e} (v + \frac{1}{2})^{2} + \omega_{e} y_{e} (v + \frac{1}{2})^{3}
$$

$$
+ \omega_{e} z_{e} (v + \frac{1}{2})^{4} + \omega_{e} a_{e} (v + \frac{1}{2})^{5},
$$



<span id="page-4-1"></span><sup>a</sup>Present work.

<span id="page-4-2"></span><sup>b</sup>Douay *et al.* (Ref. [19\)](#page-11-13).

<span id="page-4-3"></span><sup>c</sup>Chauville et al. (Ref. [6\)](#page-11-21).

<span id="page-4-4"></span><sup>d</sup>Chan *et al.* (Ref. [20\)](#page-11-20). <sup>e</sup>Roux *et al.* (Ref. [16\)](#page-11-17).

<span id="page-4-6"></span><span id="page-4-5"></span><sup>f</sup> Amiot *et al.* (Ref. [15\)](#page-11-15).

$$
B_{v} = B_{e} - \alpha_{e} (v + \frac{1}{2}) + \gamma_{e} (v + \frac{1}{2})^{2}
$$
  
+  $\delta_{e} (v + \frac{1}{2})^{3} + \varepsilon_{e} (v + \frac{1}{2})^{4}$ ,  

$$
D_{v} = D_{e} + \beta_{e} (v + \frac{1}{2}) + \zeta_{e} (v + \frac{1}{2})^{2},
$$
  

$$
q_{v} = q + \alpha^{q} (v + \frac{1}{2}).
$$

The matrix elements of the effective *N* <sup>2</sup> Hamiltonian for the  $a^3\Pi_u$  and  $b^3\Sigma_g^-$  states using Hund's case (a) basis functions  $0 = \begin{vmatrix} 3\pi/2, & 1 \\ 0, & 1 \end{vmatrix} = \begin{vmatrix} 3\pi/2, & 2\pi/2 \\ 0, & 3\pi/2 \end{vmatrix}$ ,  $3 = \begin{vmatrix} 3\pi/2, & 4\pi/2 \\ 0, & 4\pi/2 \end{vmatrix}$  and  $5 = \left(\frac{3}{2} \sum_{i=1}^{n} f \right)$  are the same as those of Merer and Brown,<sup>[24](#page-11-25)</sup> and Brazier *et al.*, [25](#page-11-26)

$$
H(0,0) = T_e + G_v - A_v + \frac{2}{3}\lambda_v + (B_v - A_{Dv} + \frac{2}{3}\lambda_D)(x+2) - D_v(x^2 + 6x + 4)
$$
  
+  $H_v(x^3 + 12x^2 + 24x + 8) \mp [o_v + o_D(x+2) + p_v + 2p_D(x+1) + q_v + q_{Dv}(3x+2)]$ ,  

$$
H(1,1) = T_e + G_v - \frac{4}{3}\lambda_v + (B_v - \frac{4}{3}\lambda_D)(x+2) - D_v(x^2 + 8x) + H_v(x^3 + 18x^2 + 16x)
$$
  
+  $\frac{1}{2}[2p_Dx + q_vx + q_{Dv}x(x+6)]$ ,  

$$
H(2,2) = T_e + G_v + A_v + \frac{2}{3}\lambda_v + (B_v + A_{Dv} + \frac{2}{3}\lambda_D)(x-2) - D_v(x^2 - 2x) + H_v(x^3 - 4x)
$$
,  

$$
H(0,1) = -\sqrt{2x} \{B_v - \frac{1}{2}A_{Dv} - \frac{1}{3}\lambda_D - 2D_v(x+2) + H_v(3x^2 + 16x + 8)
$$
  
+  $\frac{1}{2}[o_D + p_v + p_D(x+3) + 2q_v + q_{Dv}(3x+4)]\}$ ,  

$$
H(0,2) = -\sqrt{x(x-2)} \{2D_v - H_v(6x+4) \pm \frac{1}{2}[p_D + q_v + q_{Dv}(x+2)]\}
$$
,  

$$
H(1,2) = -\sqrt{2(x-2)} [B_v + \frac{1}{2}A_{Dv} - \frac{1}{3}\lambda_D - 2D_vx + H_v(3x^2 + 4x) \mp \frac{1}{2}q_{Dv}x]
$$
,  

$$
H(3,3) = T_e + G_v + B_vx - D_v(x^2 + 4x) + H_v[x^3 + 4(3x^2 + 2x)] + \frac{2}{3}\lambda_v + \frac{2}{3}\lambda_Dx - \gamma_v - 3\gamma_Dx
$$
,  

$$
H(4,4) = T_e + G_v + B_v(x+2) - D_v(x^2 + 8x + 4) + H_v(x^3 + 18x^2 + 28x + 8)
$$
  
-  $\$ 

where *A* is spin-obit constant,  $\gamma$  is spin-rotation constant,  $\lambda$  is spin-spin interaction constant, *<sup>o</sup>*, *<sup>p</sup>*, and *<sup>q</sup>* are Λ-type doubling constants, and *H* is a higher order centrifugal distortion constant. These parameters are further expanded by vibrational quantum number  $(v + 1/2)$  as

$$
H_{v} = H + \eta_{e} (v + \frac{1}{2}),
$$
  
\n
$$
A_{v} = A + \alpha^{A} (v + \frac{1}{2}) + \gamma^{A} (v + \frac{1}{2})^{2},
$$
  
\n
$$
A_{Dv} = A_{D} + \beta^{AD} (v + \frac{1}{2}) + \zeta^{AD} (v + \frac{1}{2})^{2},
$$
  
\n
$$
\lambda_{v} = \lambda + \alpha^{A} (v + \frac{1}{2}),
$$
  
\n
$$
\gamma_{v} = \gamma + \alpha^{\gamma} (v + \frac{1}{2}) + \delta^{\gamma} (v + \frac{1}{2})^{2},
$$
  
\n
$$
\rho_{v} = \rho + \alpha^{P} (v + \frac{1}{2}) + \gamma^{P} (v + \frac{1}{2})^{2},
$$
  
\n
$$
q_{v} = q + \alpha^{q} (v + \frac{1}{2}) + \gamma^{q} (v + \frac{1}{2})^{2} + \delta^{q} (v + \frac{1}{2})^{3},
$$
  
\n
$$
= q_{D} + \beta^{q} (v + \frac{1}{2}) + \zeta^{q} (v + \frac{1}{2})^{2} + \theta^{q} (v + \frac{1}{2})^{3}
$$

The spin-orbit interaction between the  $b^3 \Sigma_g^-$  and  $X^1 \Sigma_g^+$  states is expressed as  $16$ 

$$
\langle \begin{aligned} \n\langle \Sigma_{0e}^- | \mathbf{H} | \mathbf{L}_{0e}^+ \rangle &= A + A_1 (x + 2) + A_2 x, \\ \n\langle \mathbf{L}_{0e}^- | \mathbf{H} | \mathbf{L}_{0e}^+ \rangle &= -2A_1 \sqrt{x}, \n\end{aligned}
$$

where

 $q$ <sub>Dν</sub>

$$
A = \left\langle b^{3} \Sigma_{g} \middle| H_{so} \left| X^{1} \Sigma_{g}^{+} \right\rangle = A_{bX} \left\langle v_{b} \middle| v_{X} \right\rangle.
$$

 $\langle v_b|v_x\rangle$  is an overlap integral and is calculated with Le Roy's "RKR" and "LEVEL" programs.<sup>[26](#page-11-27)</sup>  $A_1$  and  $A_2$  represent effective second-order interaction constants. We set  $A_1$  to a constant  $A<sub>bXD</sub>$  in the analysis without considering  $A<sub>2</sub>$ , which cannot be determined independently as shown in Ref. [16.](#page-11-17)

The least-squares fitting with 82 molecular constants was carried out simultaneously for the 6229 transitions of the Ballik-Ramsay system and the Phillips system with a standard deviation 0.0037 cm<sup>−</sup><sup>1</sup> for the residuals. The molecular constants obtained and a comparison with the previous work is shown in Table [II.](#page-6-0)

In Amiot *et al.*'s analysis,<sup>[15](#page-11-15)</sup> a different Hamiltonian for the  ${}^{3}$ II state (from Zare *et al.*<sup>[27](#page-11-28)</sup> based on  $R$ <sup>2</sup>) was used: the main difference is that the diagonal matrix elements are all one  $B_v$  constant smaller than for the  $N^2$  Brown and Merer<sup>[24](#page-11-25)</sup> Hamiltonian that we used. Since the resulting energy of the <sup>3</sup> $\Pi$  state should be the same for both definitions, the one  $B_v$ difference in the expression for the diagonal matrix elements makes the  $T_e$  values differ by one  $B_v$  for the two definitions, that is, the  $T_e$  value for Zare *et al.*'s expression is one  $B_v$ constant (about 1.63 cm<sup>-1</sup> for the  $a^3\Pi_u$  state) larger than the value for Brown and Merer's expression, if higher-order terms are neglected. This also affects the values of other constants slightly: for example, the two definitions yield  $\omega_e$  and  $\omega_e x_e$ that differ by one  $\alpha_e$  and one  $\gamma_e$ , respectively. For this reason, we have to be careful to use the same definition when we compare our  $T_e$  values for the  $a^3\Pi_u$  state with Amiot *et al.*'s

<span id="page-6-0"></span>TABLE II. Molecular constants determined by the simultaneous analysis (in cm−<sup>1</sup> ).

		$X^1\Sigma_g^+$			$A^1\Pi_u$			
	Present work	Douay et al. <sup>19</sup>	Chan et $al.^{20}$		Present work	Douay et al. <sup>19</sup>	Chan et al. $20$	
$T_e$	$\mathbf{0}$	0	$\overline{0}$	$T_e$	8391.406 2(19)	8393.408 5(46)	8393.414 8(29)	
$\omega_e$	1855.035 2(43)	1855.014(13)	1855.066 3(63)	$\omega_e$	1608.217 8(25)	1608.199 0(52)	1608.2317(38)	
$\omega_e x_e$	13.570 1(36)	13.545(12)	13.600 7(54)	$\omega_e x_e$	12.0786(17)	12.059 7(27)	12.084 8(25)	
$\omega_e y_e$	$-0.1275(13)$	$-0.1321(50)$	$-0.1160(20)$	$\omega_e y_e$	$-0.00371(49)$	$-0.010555(39)$	$-0.00288(72)$	
$\omega_e z_e$	0.00313(20)	0.00357(89)	0.001260(32)	$\omega_e z_e$	$-0.000901(61)$		$-0.000908(90)$	
$\omega_e a_e$	$-0.001112(11)$	$-0.001$ 116(57)	$-0.001003(19)$	$\omega_e a_e$	0.0000304(28)		0.000274(41)	
$B_e$	1.820 046 5(53)	1.820 099(37)	1.820053(11)	$B_e\,$	1.6166041(51)	1.6166275(24)	1.616608(11)	
$\alpha_e \times 10^3$	17.907 5(41)	18.012(63)	17.914 3(44)	$\alpha_e \times 10^3$	16.9326(27)	16.9691(51)	16.9466(33)	
$\gamma_e \times 10^3$	$-0.1368(23)$	$-0.063(29)$	$-0.0886(17)$	$\gamma_e \times 10^3$	$-0.0527(15)$	$-0.0334(25)$	$-0.04237(95)$	
$\delta_e \times 10^3$	$-0.00094(53)$	$-0.0206(37)$	$-0.01838(21)$	$\delta_e \times 10^3$	0.00142(32)	$-0.00154(33)$	$-0.000629(81)$	
$\varepsilon_e \times 10^3$	$-0.001735(42)$			$\varepsilon_e \times 10^3$	$-0.000119(21)$			
$D_e \times 10^6$	6.9724(19)	6.964(12)	6.9526(66)	$D_e \times 10^6$	6.5056(18)	6.5086(54)	6.5005(63)	
$\beta_e \times 10^6$	0.0344(11)	0.0641(69)	0.0675(12)	$\beta_e \times 10^6$	0.02304(30)	0.0253(29)	0.0238(13)	
$\zeta_e \times 10^6$	0.00837(25)			$q \times 10^3$	$-0.19637(99)$	$-0.19676(70)$	$-0.1971(24)$	
				$\alpha^q \times 10^3$	0.00162(24)	0.00274(34)	0.00134(54) <sup>a</sup>	
				$q_D \times 10^6$	0.00505(37)		0.0061(16)	
		$a^3\Pi_u$				$b^3\Sigma_g^-$		
	Present work	Amiot et al. <sup>15</sup>	Tanabashi et al. <sup>28</sup>		Present work	Amiot et al. <sup>15</sup>	Roux et al. <sup>16</sup>	
$T_e$	720.008 3(21)	716.685 6(12) <sup>b</sup>		$T_e\,$	$(6439.08382(58))$ <sup>c</sup>	6435.736(21)		
				$\Delta T_e$	5719.075 52(58)	(5719.050(21)) <sup>d</sup>	5719.096 8(10) <sup>e</sup>	
$\omega_e$	1641.326 48(77)	1641.358 8(24)	1641.341(23)	$\omega_e$	1470.365 02(68)	1470.415(13)	1470.374(7)	
$\omega_e x_e$	11.649 04(36)	11.664 72(72)	11.6580(58)	$\omega_e x_e$	11.135 54(35)	11.154 9(42)	11.143(3)	
$\omega_e y_e$	$-0.002091(48)$		$-0.00083(41)$	$\omega_e y_e$ $\omega_e z_e$	0.010672(69) 0.0001991(45)	0.01391(38)	0.0128(4)	
$B_e$	1.632 314 2(34)	1.632 532 3(36)	1.63235(4)	$B_e$	1.498 664 7(34)	1.498 643 1(37)	1.49864(5)	
$\alpha_e \times 10^3$	16.5417(13)	16.5452(46)	16.57(3)	$\alpha_e \times 10^3$	16.287 47(58)	$16.312\ 1(26)$	16.29(3)	
$\gamma_e \times 10^3$	$-0.02855(55)$	$-0.0212(12)$	$-0.027(5)$	$\gamma_e \times 10^3$	$-0.01102(16)$	$-0.00461(38)$	$-0.009(5)$	
$\delta_e \times 10^3$	$-0.000918(68)$			$\delta_e \times 10^3$	0.000436(13)			
$D_e \times 10^6$	6.4488(18)	6.4375(20)	6.2174(22)	$D_e \times 10^6$	$6.221\,0(18)$	6.19577(41)	6.200(8)	
$\beta_e \times 10^6$	0.01471(30)	0.00517(28)		$\beta_e \times 10^6$	0.01115(14)	0.00662(31)	$-0.015(8)$	
$\zeta_e \times 10^6$	$-0.000861(87)$	0.00230(56)		$\zeta_e \times 10^6$	$-0.000267(26)$	0.000478(49)		
$H \times 10^{12}$	6.82(26)	2.916(69)	$6.745(77)^f$	$H \times 10^{12}$	4.88(27)		2.3(9)	
$\eta_e \times 10^{12}$		$-0.631(63)$						
$\boldsymbol{A}$	$-15.27750(36)$	$-15.2723(28)$	$-15.2770(3)$	$A_{bX}$	6.3331(71)		$5.65(38)^8$	
$\alpha^A$	0.01651(13)	0.0185(21)	0.0160(4)	$A_{bXD} \times 10^3$	$-0.0433(28)$		$0.08(6)^{g}$	
$\gamma^A$			0.00036(7)					
$A_D \times 10^3$	0.2344(23)	0.3906(46)	$0.2388(33)^f$					
$\beta^{AD} \times 10^3$	$-0.03143(61)$	$-0.0271(73)$						
$\zeta^{AD} \times 10^3$		0.00046(22)						
$\lambda$	$-0.15466(33)$	$-0.1563(21)$	$-0.15490(25)^f$	$\lambda$	0.15889(23)	0.1548(24)	0.1529(18)	
$\alpha^{\lambda}$	0.00030(12)	$-0.00338(84)$		$\alpha^{\lambda}$	$-0.000306(71)$		$-0.003$ 15(75)	
$\lambda_D \times 10^3$	0.00143(15)							
$\cal O$	0.67702(32)	0.6781(18)	$0.675\ 39(20)^f$	$\gamma \times 10^3$	$-1.498(12)$	$-1.429(28)$	$-1.7(6)^f$	
$\alpha^o \times 10^3$	$-4.81(11)$	$-7.1(11)$		$\alpha^{\gamma} \times 10^3$	$-0.0473(20)$	$-0.173(26)$		
$\rho_D \times 10^3$	$-0.00244(16)$		$-0.787(58)^f$	$\delta^{\gamma} \times 10^3$		0.0189(42)		
$p \times 10^3$	2.170(15)	4.25(37)	$2.465(24)^f$	$\gamma_D \times 10^6$	0.0215(27)			
$\alpha^p \times 10^3$	0.3299(46)	0.56(24)						
$p_D \times 10^6$	$-0.1348(49)$		$0.063(14)^f$					
$q \times 10^3$	$-0.5000(12)$	$-1.020(13)$	$-0.5319(20)^f$					
$\alpha^q \times 10^3$	$-0.0589(23)$	$-0.063(21)$						
$\gamma^q \times 10^3$	0.0058(12)							
$\delta^q \times 10^3$	$-0.00285(18)$							
$q_D \times 10^6$	0.01672(44)							

TABLE II. (*Continued.*)



<span id="page-7-0"></span><sup>a</sup>Corrected sign due to the different definition.

<span id="page-7-1"></span><sup>b</sup>Converted by 718.318 1(12) cm<sup>-1</sup>- $B_e(a^3\Pi_u)$  with Brown and Merer's <sup>3</sup> $\Pi$  Hamiltonian; see text for details.

<span id="page-7-2"></span><sup>c</sup>Derived value from  $\Delta T_e(b^3\Sigma_g^- - a^3\Pi_u) + T_e(a^3\Pi_u)$ .

<span id="page-7-3"></span><sup>d</sup>Derived value from  $T_e(b^3\Sigma_g^-)$ – $T_e(a^3\Pi_u)$ .

<span id="page-7-4"></span><sup>e</sup>Converted by  $\Delta T_0(b^3\Sigma_g^- - a^3\Pi_u) - G_0(b^3\Sigma_g^-) + G_0(a^3\Pi_u) + B_e(a^3\Pi_u)$ , where  $\Delta T_0(b^3\Sigma_g^- - a^3\Pi_u) = 5632.1039(10)$  cm<sup>-1</sup> and the molecular constants in  $a^3\Pi_u$  were taken from Amiot *et al.*[15](#page-11-15)

<span id="page-7-5"></span>f Value of the effective constant in  $v = 0$ .

<span id="page-7-6"></span><sup>g</sup>Averaged value for different vibrational states. See text for details.

value:[15](#page-11-15) our value is 721.64 cm−<sup>1</sup> compared to Amiot *et al.*'s 718.32 cm−<sup>1</sup> using Zare *et al.*'s definition, or 720.01 cm−<sup>1</sup> versus Amiot *et al.*'s 716.69 cm<sup>−</sup><sup>1</sup> using Brown and Merer's definition. In both cases, our value of  $T_e$  is 3.32 cm<sup>-1</sup> larger than that of Amiot *et al.*[15](#page-11-15) It should be emphasized that both the *N* 2 and *R* 2 rotational Hamiltonians are effective Hamiltonians and, for example, the  $T_e$  values both include a  $B \langle L^2 \rangle$  contribution.

Since the energy difference  $\Delta T_e$  ( $b^3 \Sigma_g^- - a^3 \Pi_u$ ) is determined directly from the observed spectrum, the values of  $\Delta T_e$  $(b^3\Sigma_g^- - a^3\Pi_u)$  should be similar for different analyses (Amiot *et al.*, [15](#page-11-15) Roux *et al.*, [16](#page-11-17) and the present work) using the same definition of the Hamiltonian. Consequently, the values of *T*<sup>e</sup>  $(b<sup>3</sup>\Sigma<sub>g</sub><sup>-</sup>)$  are also different, as shown in Table [II.](#page-6-0)

The off diagonal spin-orbit interaction constant *AbX* = 6.333(7) cm<sup>-1</sup> between  $b^3 \Sigma_g^-$  and  $X^1 \Sigma_g^+$  is comparable with the average value of 5.7(4) cm<sup>-1</sup> obtained from 5.05, 5.62 the average value of  $5.7(4)$  cm<sup>-1</sup> obtained from 5.05, 5.62, 6.03, and 5.90 cm<sup>−</sup><sup>1</sup> , which are converted from the previously determined spin-orbit interactions<sup>[15](#page-11-15)</sup>  $A_{bX}$   $\langle v_b | v_X \rangle = 2.36(12)$ ,  $2.73(6)$ ,  $2.05(5)$ , and  $0.82(2)$  cm<sup>-1</sup> and the present values of the vibrational overlap integrals  $\langle v_b|v_x\rangle = 0.467, 0.486, 0.340,$ and 0.139 between the vibrational states  $v_b-v_x = 0-3$ , 1-4, 2-5, and 3-6, respectively, which are similar to the values of  $\langle v_b|v_X\rangle$ calculated by Davis *et al.*[18](#page-11-19)

<span id="page-7-8"></span>Inclusion of several small molecular constants,  $\gamma^A$  and<br>for  $a^3\Pi$  and  $\delta\chi$  for  $b^3\Sigma$  = in the least-squares fitting did  $\frac{1}{2}$  and  $\frac{1}{2}$  a  $^{AD}$  for  $a^3\Pi_\text{u}$ , and  $\delta^\gamma$  for  $b^3\Sigma_g^-$ , in the least-squares fitting did<br>of improve the overall standard deviation significantly and made other constants uncertain due to parameter correlation; they were set to zero in the final analysis. For the  $a^3\Pi_u$  state up to  $v = 4$ , many higher-order expansions of the  $\Lambda$ -type doubling constants  $q_v$  and  $q_{Dv}$  with a slow convergence in the  $(v + 1/2)^n$  dependence, as shown in Table [II,](#page-6-0) are required for the fit even when we remove the bands associated with v  $= 4$  of  $a^3\Pi_u$ , which may indicate that there are some small perturbations from other states, probably  $v = 0$  of the  $c^3 \Sigma_u^+$ state as seen in Fig. [1.](#page-3-0) The  $v = 5$  and 6 of  $a^3\Pi_u$  bracket v  $= 0$  of  $c^3 \Sigma_u^+$  in energy, and much more prominent perturbations with opposite directions for the frequency shifts for the bands associated with  $v = 5$  and 6 of  $a^3\Pi_u$ , as shown in the supplementary material, $^{23}$  $^{23}$  $^{23}$  may be explained by the interactions among the three states, which will be discussed in a future paper.

### **IV. LEVEL CROSSINGS FOR POTENTIAL FORBIDDEN TRANSITIONS**

By setting the spin-orbit interaction constants  $A_{bX}$  and  $A<sub>bXD</sub>$  to zero, we can calculate the frequency shifts due to the spin-orbit interaction, i.e., the magnitude of the perturbation. In Table [III,](#page-8-0) we list the lines with perturbations larger than 0.1 cm<sup>−</sup><sup>1</sup> . These perturbed lines were all known from previous studies<sup>[15](#page-11-15)</sup> except for the lines involved with the energy level crossing at  $J = 2$  for  $v = 3(F_1)$  of  $b^3 \Sigma_g$ <sup>-</sup> and  $v = 6$  of  $X^1 \Sigma_g$ <sup>+</sup> (Fig. [2\)](#page-7-7), which was thought previously to have a crossing only at  $J < 0$  (in other words, not strongly perturbed). For example, the assigned transition for  $J = 3-2$  and  $v = 4-6$  of the Phillips system by Douay *et al.*<sup>[19](#page-11-13)</sup> showed no perturbation.

With the calculation in the present analysis, the energy difference at  $J = 2$  between  $v = 3(F_1)$  of  $b^3 \Sigma_g$ <sup>-</sup> and  $v = 6$  of  $X^1\Sigma_g^+$  is only 0.07 cm<sup>-1</sup> without considering the spin-orbit interaction, and the two energy levels are shifted apart by about  $\pm 0.5$  cm<sup>-1</sup> with the 0.89 cm<sup>-1</sup> spin-orbit interaction. This nearly degenerate perturbation makes the wave functions of the singlet and triplet states mix almost completely, which should result in the corresponding forbidden transitions having

<span id="page-7-7"></span>

FIG. 2. Plot of the calculated term energies of  $X^1\Sigma_g^+$  ( $v = 6$ ) and  $b^3\Sigma_g^-$  ( $v = 3$ ) ye, retational quantum number *L*. The term energies house 1.7  $I(L, 1)$  $=$  3) vs. rotational quantum number *J*. The term energies have  $1.7J(J+1)$ subtracted to make the  $X^{1}\Sigma_{g}^{+}$  ( $v = 6$ ) curve close to a horizontal line. The layer crossing occurs at  $I = 2$  of  $h^{3}\Sigma^{-} = v = 3$  (E) and at  $I = 14$  of  $h^{3}\Sigma^{-} = v$ level crossing occurs at  $J = \tilde{2}$  of  $b^3 \Sigma_g^-$  v = 3 (F<sub>1</sub>) and at  $J = 14$  of  $b^3 \Sigma_g^-$  v = 2 (E<sub>2</sub>) with  $X^1\Sigma^+$  v = 6  $= 3$  (F<sub>3</sub>) with  $X^1\Sigma_g^+$  v = 6.

<span id="page-8-0"></span>TABLE III.  $C_2$  transitions with perturbations larger than 0.1 cm<sup>-1</sup>.



TABLE III. (*Continued.*)

$v'$ - $v''$	$J'-J''$	Observed	$O-C$	$\Delta^{\mathbf{a}}$	$v'$ - $v''$	$J'-J''$	Observed	$O-C$	$\Delta^{\mathbf{a}}$	
Ballik-Ramsay system $b^3\Sigma_g^- - a^3\Pi_u$					Forbidden transitions $X^1\Sigma_g^+ - a^3\Pi_u$					
$2 - 1$	$26(F_1) - 25(F_1)$	6874.5727	0.0018	0.1020	$6 - 2$	$14-14(F_3)$	6662.2830	0.0038	0.1560	
$2 - 1$	$26(F_1) - 26(F_1)$	6794.7030	$-0.0060$	0.1020	$6 - 2$	$14-15(F_3)$	6612.1625	$-0.0002$	0.1560	
$2 - 1$	$26(F_1) - 26(F_2)$	6709.0289	$-0.0019$	0.1020	$6 - 4$	$14-13(F_3)$	3597.8123	$-0.0003$	0.1560	
$2 - 1$	$26(F_1) - 27(F_1)$	6711.2885	$-0.0023$	0.1020	$6 - 4$	$14-14(F_3)$	3550.9110	0.0029	0.1560	
$2 - 2$	$26(F_1) - 27(F_1)$	5128.2777	$-0.0030$	0.1020						

<span id="page-9-0"></span><sup>a</sup>Frequency shift due to the spin-orbit interaction between the  $X^1\Sigma_g^+$  and  $b^3\Sigma_g^-$  states.

<span id="page-9-1"></span>

FIG. 3. Forbidden transitions due to the energy level crossing. The upper forbidden transition is associated with the allowed transition of the Phillips system, and the lower forbidden transition is associated with the allowed transition of the Ballik-Ramsay system.

similar intensities to the allowed ones. According to the deperturbation analysis, at the level crossing for  $J = 2$ , the mixed wave functions have a 57% contribution from the parent state and a 43% contribution from the perturber. Therefore, the intensity borrowing from the allowed transition makes the forbidden transition in Fig. [3](#page-9-1) have an intensity ratio of  $43\%:57\% = 0.75.$ 

<span id="page-9-2"></span>

FIG. 4. A portion of the Fourier transform emission spectrum taken from Ref. [21.](#page-11-22) The strong lines marked with  $\Box$  belong to the v = 0-0 band of the  $B^1 \Delta_g - A^1 \Pi_u$  system (Ref. [12\)](#page-11-10). The lines marked with  $\nabla$  belong to the v = 3.4 hand of the Ballik Barneav  $b^3 \Sigma = a^3 \Pi$ , avetern assigned in the v = 3-4 band of the Ballik-Ramsay  $b^3\Sigma_g^2 - a^3\Pi_u$  system assigned in the present study. The lines merked with A belong to the y = 2.4 and 3.5 hands present study. The lines marked with  $\blacklozenge$  belong to the v = 2-4 and 3-5 bands of the  $B'^{1}\Sigma_{g}^{+}$  –  $A^{1}\Pi_{u}$  system. The three lines marked with \* are forbidden<br>transitions assigned in the present study. transitions assigned in the present study.

For  $v = 3(F_3)$  of  $b^3\Sigma_g^-$  and  $v = 6$  of  $X^1\Sigma_g^+$ , a level crossing at  $J = 14$  was known previously (Fig. [2\)](#page-7-7), which has a 2.75 cm<sup>-1</sup> energy difference without considering the spin-orbit interaction. Our deperturbation analysis showed that the same 0.89 cm<sup>-1</sup> spin-orbit interaction makes the energy levels shift apart by about  $\pm 0.15$  cm<sup>-1</sup>, and the intensity borrowing from<br>the allowed transitions makes the forbidden transitions have an the allowed transitions makes the forbidden transitions have an intensity ratio of 0.06.

The level crossing at  $J = 52$  for  $v = 1(F_3)$  of  $b^3\Sigma_g^-$  and  $v = 4$  of  $X^1\Sigma_g^+$  has a 1.45 cm<sup>-1</sup> energy difference without considering the spin-orbit interaction, and the levels are shifted apart by about  $\pm 1.5$  cm<sup>-1</sup> with the 3.06 cm<sup>-1</sup> spin-orbit interaction. According to the deperturbation analysis on this interaction. According to the deperturbation analysis on this level crossing, the wave functions are a 75%:25% mixture,

<span id="page-9-3"></span>

FIG. 5. Two short sections of spectra, (a) and (b), that show forbidden transitions and corresponding allowed transitions. The symbols have the same meaning as in Fig. [4.](#page-9-2)

<span id="page-10-0"></span>

FIG. 6. More forbidden transitions and corresponding allowed transitions. The intensity scale in (b) has been magnified by five times relative to the intensity scale in (a). The lines marked with x belong to the  $A^2\Pi - X^2\Sigma^+$ transitions of the carbon phosphide (CP) radical (Ref. [30\)](#page-11-29).

which leads to an intensity ratio of 0.33 for the forbidden to the allowed transitions. However, the assignment for  $J = 52$ - $52(F_3)$  of v = 1-0 and 1-1 bands in the Ballik-Ramsay system by Roux *et al*.<sup>[16](#page-11-17)</sup> showed a perturbation shift of 1.0 cm<sup>-1</sup>, which is inconsistent with our calculated shift of 1.5 cm<sup>−</sup><sup>1</sup> (see the supplementary material<sup>[23](#page-11-24)</sup>) and is an erroneous assignment.

### **V. ASSIGNMENT OF THE FORBIDDEN TRANSITIONS**

In Sec. [II,](#page-4-7) we have assigned several bands of the Ballik-Ramsay system by using a Fourier transform emission spectrum in the range of 1800-4000  $cm^{-1}$  with a spectral resolution of 0.02 cm<sup>-1</sup> taken previously with the discharge of a  $CH_4$  and He mixture for the study of the CH radical.<sup>[21](#page-11-22)</sup> A small portion of the spectrum (Fig. [4\)](#page-9-2) shows the strong  $v = 0$ -0 band of the  $B^1\Delta_g$ – $A^1\Pi_u$  system<sup>[12](#page-11-10)</sup> and the new v = 3-4 band<br>of the Ballik Bomsov system and the week y = 2.4 and 3.5 of the Ballik-Ramsay system and the weak  $v = 2-4$  and 3-5 bands of the  $B'^{1}\Sigma_{g}^{+}$  –  $A^{1}\Pi_{u}$  system, which will be presented<br>in enother publication. In the greature, three forbidden in another publication. In the spectrum, three forbidden transitions between  $v = 6$  of  $X^{1}\Sigma_{g}^{+}$  and  $v = 4$  of  $a^{3}\Pi_{u}^{+}$ <br>wises found at 2560,056, 2592,694, and 2501,741 am<sup>-1</sup>. The were found at 3569.956, 3583.684, and 3591.741 cm<sup>-1</sup>. The forbidden transition at 3569.956 cm<sup>-1</sup> with  $J = 2$ -2 for v = 6

<span id="page-10-1"></span>

FIG. 7. Additional forbidden transitions and corresponding allowed transitions. The intensity scale in (b) has been magnified by three times relative to the intensity scale in (a). The lines marked with  $\diamond$  belong to the Phillips  $A^1\Pi_u - X^1\Sigma_g^+$  system.

of  $X^1\Sigma_g^+$  and  $v = 4(F_2)$  of  $a^3\Pi_u$  corresponds to the allowed transition at 3571.109 cm<sup>-1</sup> for  $J = 2{\text -}2$  for  $v = 3(F_1)$  of  $b^3 \Sigma_g$ <sup>-</sup> and v = 4(F<sub>2</sub>) of  $a^3 \Pi_u$ , and is due to the strong upperlevel mixing between  $v = 6$  of  $X^1\Sigma_g^+$  and  $v = 3(F_1)$  of  $b^3\Sigma_g^-$ . This pair of allowed and forbidden transitions shows comparable intensity (Fig.  $5(a)$ ) as predicted in Sec. [IV,](#page-7-8) and the wavenumber of the forbidden transition is also consistent with the prediction to within 0.02 cm<sup>-1</sup>, which was reduced further to less than  $0.01 \text{ cm}^{-1}$  by adding this transition to the least-squares fit. Also, the forbidden transition at 3591.741 cm<sup>-1</sup> (Fig. [5\(b\)\)](#page-9-3) with  $J = 2{\text -}2$  for  $v = 6$  of  $X^{1}\Sigma_{g}^{+}$ and  $v = 4(F_1)$  of  $a^3\Pi_u$  was assigned within the predicted wavenumber range: the line is slightly weaker than the corresponding allowed transition at 3592.885 cm<sup>−</sup><sup>1</sup> with *J* = 2-2 for v = 3(F<sub>1</sub>) of  $b^3\Sigma_g^-$  and v = 4(F<sub>1</sub>) of  $a^3\Pi_u$ . By checking in the  $v = 3-2$  and 3-1 bands of the Ballik-Ramsay system in the spectrum of Ref. [19,](#page-11-13) six more forbidden transitions were assigned as listed in Table [III](#page-8-0) and two of them are shown in Fig. [6.](#page-10-0)

At the level crossing at  $J = 14$  for  $v = 3(F_3)$  of  $b^3\Sigma_g^-$  and  $v = 6$  of  $X^{1}\Sigma_{g}^{+}$ , six forbidden transitions for  $v = 6{\text -}1(\overline{F}_{3})$ , 6- $2(F_3)$ , and  $6\text{-}4(F_3)$  between  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  were assigned as listed in Table [III](#page-8-0) and the observed intensity ratios to the corresponding allowed transitions are about 10%, which are comparable to the predicted 6% intensity ratio. Fig. [7](#page-10-1) shows two of the forbidden transitions and the corresponding allowed transitions.

We also searched for forbidden transitions between  $A^1\Pi_u$ and  $b^3\Sigma_g^-$  corresponding to the allowed transitions of the Phillips system. However, due to the weak intensity of the forbidden transitions at the level crossing and the accidental disturbance by nearby strong transitions, only one such forbidden transition was identified as listed in Table [III.](#page-8-0)

The forbidden and allowed transitions involved in the level crossing at  $J = 52$  for  $v = 1$  (F<sub>3</sub>) of  $b^3 \Sigma_g$ <sup>-</sup> and  $v = 4$ of  $X^1\Sigma_g^+$  could not be assigned because only transitions with a maximum *J* value of about 37 were observed in our Fourier transform emission spectra.

### **VI. CONCLUSIONS**

A deperturbation analysis using 6229 transitions of the Ballik-Ramsay system and the Phillips system of  $C_2$  led to the determination of the energy difference between the  $X^{1}\Sigma_{g}^{+}$ <br>and  $s^{3}\Pi_{g}$  states as 720,009(2) and which is about 2.2 and  $^{-1}$ and  $a^3\Pi_u$  states as 720.008(2) cm<sup>-1</sup>, which is about 3.3 cm<sup>-1</sup> larger than the previous value. A new energy-level crossing was found at *J* = 2 between v = 3 of  $b^3\Sigma_g^-$  and v = 6<br>of  $S^1\Sigma_f^+$  where the strong only only interesting serves a of  $X^1\Sigma_g^+$ , where the strong spin-orbit interaction causes a<br>negative complete mining heterogy the wave functions of the nearly complete mixing between the wave functions of the  $b^3 \Sigma_g$  and  $X^1 \Sigma_g$ <sup>+</sup> states and forbidden transitions between the  $X^1 \Sigma_f$  + and  $a^3 \Pi_g$  states were found with similar intensity as  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  states were found with similar intensity as the corresponding allowed transitions. The observation of the forbidden transitions at the predicted line positions and intensities verifies the new value of the energy difference between the  $X^1\Sigma_g^+$  and  $a^3\Pi_u$  states. Recently, the deperturbation of the  $a^3\Sigma_g^+$  and  $a^1\Pi_u$  states by Nolssimo and Endel<sup>0</sup> the  $c^3 \Sigma_u^+$ ,  $a^3 \Pi_u$ , and  $A^1 \Pi_u$  states by Nakajima and Endo<sup>[10](#page-11-8)</sup> also required the singlet-triplet energy gap to be increased by about 3 cm<sup>-1</sup> from the literature value,<sup>[15](#page-11-15)</sup> which is consistent with our results.

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- <span id="page-11-0"></span><sup>1</sup>J. S. A. Brooke, P. F. Bernath, T. W. Schmidt, and G. B. Bacskay, [J. Quant.](http://dx.doi.org/10.1016/j.jqsrt.2013.02.025) [Spectrosc. Radiat. Transfer](http://dx.doi.org/10.1016/j.jqsrt.2013.02.025) 124, 11 (2013).
- <span id="page-11-1"></span> $2\overline{M}$ . Martin, [J. Photochem. Photobiol., A](http://dx.doi.org/10.1016/1010-6030(92)80001-C) 66, 263 (1992).
- <span id="page-11-2"></span><sup>3</sup>E. A. Ballik and D. A. Ramsay, [J. Chem. Phys.](http://dx.doi.org/10.1063/1.1730515) **31**, 1128 (1959).
- <span id="page-11-3"></span><sup>4</sup>E. A. Ballik and D. A. Ramsay, [Astrophys. J.](http://dx.doi.org/10.1086/147485) 137, 61 (1963).
- <span id="page-11-4"></span> ${}^{5}E$ . A. Ballik and D. A. Ramsay, [Astrophys. J.](http://dx.doi.org/10.1086/147486) 137, 84 (1963).
- <span id="page-11-21"></span><sup>6</sup>J. Chauville, J. P. Maillard, and A. W. Mantz, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(77)90244-2) 68, 399 (1977).
- <span id="page-11-5"></span><sup>7</sup>S. P. Davis, M. C. Abrams, J. G. Phillips, and M. L. P. Rao, [J. Opt. Soc. Am.](http://dx.doi.org/10.1364/JOSAB.5.002280) **[B](http://dx.doi.org/10.1364/JOSAB.5.002280)** 5, 2280 (1988).
- <span id="page-11-6"></span><sup>8</sup>D. L. Kokkin, N. J. Reilly, C. M. Morris, M. Nakajima, K. Nauta, S. H. Kable, and T. W. Schmidt, [J. Chem. Phys.](http://dx.doi.org/10.1063/1.2408412) 125, 231101 (2006).
- <span id="page-11-7"></span><sup>9</sup>T. W. Schmidt, "Astronomical molecular spectroscopy," in *Computational Spectroscopy: Methods, Experiments and Applications*, edited by J. Grunenberg (Wiley, Weinheim, 2010), p. 386.
- <span id="page-11-8"></span><sup>10</sup>M. Nakajima and Y. Endo, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/j.jms.2014.06.002) **302**, 9 (2014); **305**, [48](http://dx.doi.org/10.1016/j.jms.2014.10.002) (2014).
- <span id="page-11-9"></span><sup>11</sup>J. G. Phillips, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(68)90008-8) **28**, 233 (1968).
- <span id="page-11-10"></span><sup>12</sup>M. Douay, R. Nietmann, and P. F. Bernath, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(88)90237-8) **131**, 261 (1988).
- <span id="page-11-11"></span><sup>13</sup>K. Kirby and B. Liu, [J. Chem. Phys.](http://dx.doi.org/10.1063/1.437480) 70, 893 (1979).
- <span id="page-11-12"></span><sup>14</sup>P. Bornhauser, Y. Sych, G. Knopp, T. Gerber, and P. P. Radi, [J. Chem. Phys.](http://dx.doi.org/10.1063/1.3526747) 134, 044302 (2011).
- <span id="page-11-17"></span><span id="page-11-15"></span><sup>15</sup>C. Amiot, J. Chauville, and J. P. Maillard, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-285E2(79)90143-7) **75**, 19 (1979). <sup>16</sup>F. Roux, G. Wannous, F. Michaud, and J. Verges, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(85)90316-9) 109, 334 (1985).
- <span id="page-11-18"></span> $17E$ . Kagi and K. Kawaguchi, [J. Mol. Struct.](http://dx.doi.org/10.1016/j.molstruc.2006.02.026) 795, 179 (2006).
- <span id="page-11-19"></span><sup>18</sup>S. P. Davis, M. C. Abrams, Sandalphon, J. W. Brault, and M. L. P. Rao, [J.](http://dx.doi.org/10.1364/JOSAB.5.001838) [Opt. Soc. Am. B](http://dx.doi.org/10.1364/JOSAB.5.001838) 5, 1838 (1988).
- <span id="page-11-13"></span><sup>19</sup>M. Douay, R. Nietmann, and P. F. Bernath, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(88)90236-6) **131**, 250 (1988).
- <span id="page-11-20"></span><sup>20</sup>M.-C. Chan, S.-H. Yeung, Y.-Y. Wong, Y. Li, W.-M. Chan, and K.-H. Yim, [Chem. Phys. Lett.](http://dx.doi.org/10.1016/j.cplett.2004.03.139S.) 390, 340 (2004); S.-H. Yeung, Ph.D. thesis, The Chinese University of Hong Kong, Hong Kong, 2009.
- <span id="page-11-22"></span> $21P$ . N. Ghosh, M. N. Deo, and K. Kawaguchi, [Astrophys. J.](http://dx.doi.org/10.1086/307904) 525, 539 (1999).
- <span id="page-11-23"></span> $22$ W.-B. Yan, R. F. Curl, A. J. Merer, and P. G. Carrick, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(85)90174-2) 112, 436 (1985).
- <span id="page-11-24"></span><sup>23</sup>See supplementary material at [http:](http://dx.doi.org/10.1063/1.4907530)[//](http://dx.doi.org/10.1063/1.4907530)[dx.doi.org](http://dx.doi.org/10.1063/1.4907530)[/](http://dx.doi.org/10.1063/1.4907530)[10.1063](http://dx.doi.org/10.1063/1.4907530)/[1.4907530](http://dx.doi.org/10.1063/1.4907530) for the total line list used in the present analysis.
- <span id="page-11-25"></span><sup>24</sup>J. M. Brown and A. J. Merer, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(79)90172-3) 74, 488 (1979).
- <span id="page-11-26"></span><sup>25</sup>C. R. Brazier, R. S. Ram, and P. F. Bernath, [J. Mol. Spectrosc.](http://dx.doi.org/10.1016/0022-2852(86)90012-3) 120, 381 (1986).
- <span id="page-11-27"></span> ${}^{26}R$ . J. Le Roy, LEVEL 7.7: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels, University of Waterloo Chemical Physics Research Report CP-661, 2005, see [http:](http://leroy.uwaterloo.ca/programs/)[//](http://leroy.uwaterloo.ca/programs/)[leroy.](http://leroy.uwaterloo.ca/programs/) [uwaterloo.ca](http://leroy.uwaterloo.ca/programs/)[/](http://leroy.uwaterloo.ca/programs/)[programs](http://leroy.uwaterloo.ca/programs/)[/](http://leroy.uwaterloo.ca/programs/).
- <span id="page-11-28"></span> $27R$ . N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, [J. Mol.](http://dx.doi.org/10.1016/0022-2852(73)90025-8) [Spectrosc.](http://dx.doi.org/10.1016/0022-2852(73)90025-8) 46, 37 (1973).
- <span id="page-11-14"></span><sup>28</sup>A. Tanabashi, T. Hirao, T. Amano, and P. F. Bernath, [Astrophys. J., Suppl.](http://dx.doi.org/10.1086/510742) [Ser.](http://dx.doi.org/10.1086/510742) 169, 472 (2007).
- <span id="page-11-16"></span><sup>29</sup>M. Nakajima and Y. Endo, [J. Chem. Phys.](http://dx.doi.org/10.1063/1.4851436) 139, 244310 (2013).
- <span id="page-11-29"></span><sup>30</sup>R. S. Ram, J. S. A. Brooke, C. M. Western, and P. F. Bernath, [J. Quant.](http://dx.doi.org/10.1016/j.jqsrt.2014.01.030) [Spectrosc. Radiat. Transfer](http://dx.doi.org/10.1016/j.jqsrt.2014.01.030) 138, 107 (2014).