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Laser-induced breakdown spectra of Zn_2 molecule in the violet region

SUBHASH C SINGH, K S OJHA and R GOPAL
Laser & Spectroscopy Laboratory, Department of Physics, University of Allahabad, Allahabad 211 002, India
E-mail: spectra2@rediffmail.com

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Abstract. Laser-induced breakdown spectrum has been recorded in the region of 380–455 nm using second harmonics of Nd:YAG laser, computer-controlled TRIAX 320 M monochromator with a reciprocal linear dispersion 2.64 nm/mm fitted with ICCD detector. The spectrum consists of 108 bands, which are classified into four new subsystems $E0_u^+ (^1\Sigma_u^+) \rightarrow A1_g(^3\Pi_g)$, $J0_g^{\pm}\backslash 1_g(^3\Sigma_g^+) \rightarrow D1_u(^1\Pi_u)$, $F1_u \rightarrow A0_g^{\pm}(^3\Pi_g)$ and $F1_u \rightarrow A2_g(^3\Pi_g)$ along with additional bands of the known system $E0_u^+(^1\Sigma_u^+) \rightarrow A0_g^{\pm}(^3\Pi_g)$. The molecular constants for these systems have also been determined.

Keywords. Laser-induced breakdown spectra; spectra of diatomic molecule; molecular spectra; Zn_2 spectra.

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1. Introduction

The study of excimer and van der Waals molecules such as Hg_2, Cd_2 and Zn_2 are of current interest as they are potential candidates for the possible development of new high power excimer lasers. Group IIB metal dimers (Hg_2, Cd_2 and Zn_2) have essentially repulsive ground states with very shallow van der Walls minima. Lasing action takes place due to the 'bound-continuum' transition while dissociative ground state is important for attaining the condition of population inversion.

Winans [1] has observed absorption spectrum of zinc molecule for the first time while emission spectrum has been reported by Winans [2] and Hamada [3] and recorded three band maxima of zinc molecule lying at 368.0, 378.8 and 475.0 nm using hollow cathode discharge. Ault and Andrews [4] have studied $^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition of Zn_2 in the UV region. Czajkowski *et al* [5] have reported excitation spectrum of Zn_2 molecule in the 305–310 nm region using pulsed dye laser crossing supersonic molecular beam and have provided information about ground state $X0_g^+(^1\Sigma_g^+)$ and $0_u^+(^3\Pi_u)$ excited state. Hay *et al* [6], Bender *et al* [7] and Couty *et al* [8] have used configuration interaction (CI) calculation to calculate potential energy

curves of these dimers and suggested that most of the excited states of zinc dimer are attractive with repulsive ground state $X0_g^+(^1\Sigma_g^+)$. In recent years Kedzierski *et al* [9–15] have recorded six band systems of Zn_2 molecule in the UV region using pump and probe method. Kedzierski *et al* have also recorded excitation spectra of Zn_2 molecule in the 628–720 nm [9], 530–570 nm [10] and 420–470 nm region [11], out of which the last one is assigned as $0_u^+(^1\Sigma_u^+) \leftarrow {}^3\Pi_g$ transition. Singh *et al* [16] have reported two new band systems of Zn_2 molecule in the 480–520 nm region using laser-induced breakdown spectroscopy. The present paper deals with the new findings of laser-induced breakdown spectrum of Zn_2 molecule in the 380–455 nm region.

2. Experimental

The experimental set-up consists of Spectra Physics pulsed Nd:YAG laser with second harmonics at repetition rate 10 Hz, 10″ diameter cylindrical ablation chamber with quartz windows and a computer controlled Spex TRIAX 320 M monochromator fitted with TE cooled ICCD detector system. The zinc rod (Spec-pure Johnson Mathey) is mounted inside a laser ablation chamber filled with argon gas at 1 Torr pressure after evacuating it up to 10^{-3} Torr by using rotary pump. The zinc plasma is produced focusing 532 nm of Nd:YAG laser beam of 35 mJ. The zinc target is continuously rotating and translating in such a way that each laser pulse falls on a fresh surface with the help of a stepper motor. Radiation from the plasma is focused on the entrance slit of the monochromator using a cylindrical lens of focal length 25 cm. The produced plasma is allowed to cool adiabatically for about 60–240 ns using delay time for ICCD gating. The ICCD signals are sent to the computer using SpectraMax software for data acquisition and Galactic Grams 32 software is used for peak marking, spectral analysis etc. The experimental set-up for recording laser-induced breakdown spectrum is shown in figure 1.

3. Results and discussion

The recorded laser-induced breakdown spectrum of Zn_2 molecule in the region of 380–452 nm consists of 108 new bands in addition to the bands reported by Kedzierski *et al* [11] in the same region. All these bands are classified into two systems along with the already existing system. Descriptions of these band systems are as follows:

3.1 *Spectrum of* $E0_u^+(^1\Sigma_u^+) \rightarrow A0_g^{\pm}$, $1_g(^3\Pi_g)$ *transition*

This band system lies in the region of 425–455 nm and the observed 34 red degraded bands are assigned to two subsystems $E0_u^+(^1\Sigma_u^+) \rightarrow A0_g^+(^3\Pi_g)$ and $E0_u^+(^1\Sigma_u^+) \rightarrow A1_g(^3\Pi_g)$. Kedzerski *et al* [10,11], with the analogy of Cd_2 [7] calculations, suggested that $A^3\Pi_g$ state splits into four components given as $\Omega = 0_g^{\pm}$, 1_g and 2_g while $E^1\Sigma_u^+$ has $\Omega = 0_u^+$ component. Electronic transitions $0_u^+ \rightarrow 0_g^+$ and

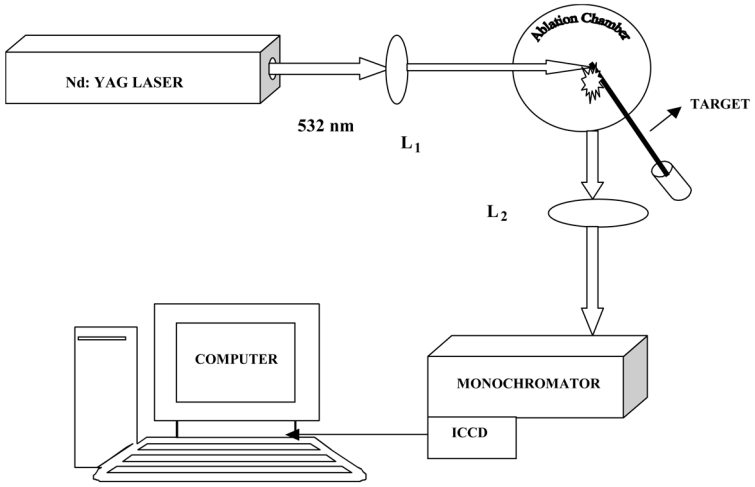

Figure 1. Experimental set-up.

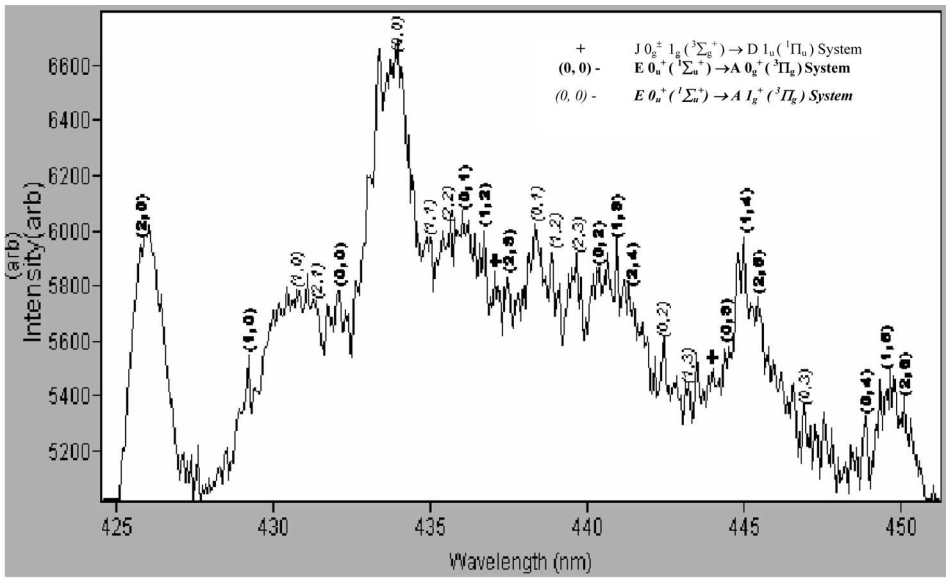

Figure 2. LIBS of E → A transition of Zn_2 molecule.

$0_u^+ \rightarrow 1_g$ are allowed according to the selection rule $\Delta\Omega = 0, \pm 1$. The transition $0_u^+ \rightarrow 0_g^+$ was observed by Kedzerski *et al* [11] while $0_u^+ \rightarrow 1_g$ transition is observed for the first time by the authors. These two subsystems are displayed in figure 2 and their descriptions are given below.

Table 1. Bandhead data of $E0_u^+(^1\Sigma_u^+) \rightarrow A0_g^+(^3\Pi_g)$ transition of Zn_2 molecule.

v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)	v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)
0,0	23136.2*	23141.6	4,6	22594.5	22576.6
1,1	23105.2*	23104.0	0,3	22493.6*	22493.6
2,2	23067.9	23065.8	1,4	22465.0*	22465.0
0,1	22921.5*	22922.6	2,5	22442.9	22435.8
1,2	22927.2*	22888.0	3,6	22406.6	22406.0
2,3	22891.5	22852.8	4,7	22371.0	22375.6
3,4	22817.8	22817.0	0,4	22271.4*	22283.6
0,2	22704.9*	22706.6	1,5	22250.0*	22258.0
1,3	22672.4*	22675.0	2,6	22225.53	22231.8
2,4	22642.7	22642.8	1,0	23292.6	23323.0
3,5	22609.4	22610.0	2,0	23468.7	23500.8

*Bands reported by Kedzereski *et al* [10].

3.1.1 *Spectrum of* $E0_u^+(^1\Sigma_u^+) \rightarrow A0_g^+(^3\Sigma_g)$ *transition*

Twenty-two red degraded bands are assigned to $E(0_u^+) \rightarrow A(0_g^+)$ transition along with 11 bands already reported by Kedziereski *et al* [11] in this region. All these bands are attributed to $\Delta v = 0, \pm 1, \pm 2, -3$ and -4 sequences. Bandhead data along with their assignments are given in table 1. The molecular constants obtained are almost the same as given by Kedziereski *et al* [11] and these are

$$\nu_{00} = 23141.6 \text{ cm}^{-1}, \quad \omega_e' = 185.0, \quad \omega_e' x_e' = 1.80,$$
$$\omega_e'' = 222.0, \quad \omega_e'' x_e'' = 1.50.$$

3.1.2 *Spectrum of* $E0_u^+(^1\Sigma_u^+) \rightarrow A1_g(^3\Pi_g)$ *transition*

This new system lying in the region of 430–450 nm consists of 16 red degraded bands with (0,0) band at 23027.6 cm^{-1}. All these bands are assigned to $\Delta v = 0, \pm 1, -2, -3$ and -4 sequences. The bandhead data and their assignments are presented in table 2. Molecular constants evaluated for $0_u^+ \rightarrow 1_g$ and $0_u^+ \rightarrow 0_g^+$ transitions are found to be the same.

It was earlier estimated by Kedziereski *et al* [10] that the separation between $0_g^\pm$ and 1_g states of Zn_2 is 130 cm^{-1} and that of 1_g and 2_g states is 170 cm^{-1}. The transition $0_u^+ \rightarrow 0_g^+$ has been reported earlier by Kedziereski *et al* [11] while $0_u^+ \rightarrow 1_g$ transition is new. Kedziereski *et al* [10] on the basis of Boltzmann factor have suggested that the probabilities of transitions from $E0_u^+(^1\Sigma_u^+)$ state to $A0_g^+(^3\Pi_g)$ and $A1_g(^3\Pi_g)$ states should be in the ratio of 1 : 1.7. The intensities and separation between two (0,0) bands of $0_u^+ \rightarrow 0_g^+$ and $0_u^+ \rightarrow 1_g$ transitions observed during the present study are in agreement with the theoretical estimation made by Kedziereski

Table 2. Bandhead data of $E0_u^+(^1\Sigma_u^+) \rightarrow A1_g^+(^3\Pi_g)$ transition of Zn_2 molecule.

v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)	v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)
0,0	23027.56	23027.6	1,3	22561.3	22561.0
1,1	22988.9	22990.0	2,4	22524.8	22528.8
2,2	22951.4	22951.6	0,3	22367.6	22379.6
0,1	22805.9	22808.6	1,4	22351.4	22351.0
1,2	22778.9	22774.0	2,5	22322.4	22321.8
2,3	22737.9	22738.8	1,0	22209.0	22209.0
3,4	22700.8	22703.0	2,1	23171.1	23167.8
0,2	22594.6	22592.6	2,0	23390.7	23386.8

et al [10,11]. Thus the assignments of the transitions made by authors for both subsystems are justified.

3.2 *Spectrum of* $J0_g^{\pm}$, $1_g(^3\Sigma_g^+) \rightarrow D1_u(^1\Pi_u)$ *transition*

The spectrum lying in the region of 434–452 nm is assigned to one of the $J0_g^{\pm}$, $1_g(^3\Sigma_g^+) \rightarrow D1_u(^1\Pi_u)$ transitions. Twenty-four new violet degraded bands are attributed to $\Delta v = 0$, ± 1, ± 2 and ± 3 sequences of this subsystem. According to the potential energy diagram given by Hay *et al* [6] and Couty *et al* [8], T_e values for $D1_u(^1\Pi_u)$ state arising from $4\ ^1P + 4\ ^1S$ lie at 36619.6 cm^{-1} while that one of the $J0_g^{\pm}$, $1_g(^3\Sigma_g^+)$ states arising from $4\ ^3P + 4\ ^3P$ lie at 58999.6 cm^{-1}. The difference of these potential energy values is nearly equal to the ν_{00} value of the present system. Thus the present band system may be assigned to one of the $J0_g^{\pm}$, $1_g(^3\Sigma_g^+) \rightarrow D1_u(^1\Pi_u)$ transitions. The values of vibrational constants for $D(^1\Pi_u)$ and $J(^3\Sigma_g^+)$ states determined in the present case are almost the same as those reported by Kedziereski *et al* [9,15]. Table 3 is a collection of bandhead data with their classification and figure 3 shows the spectrum for the band system $J \rightarrow D$. Molecular constants determined are:

$$\nu_{00} = 22546.6\ cm^{-1}, \quad \omega_e' = 161.0, \quad \omega_e' x_e' = 0.75,$$
$$\omega_e'' = 146.7, \quad \omega_e'' x_e'' = 1.90.$$

3.3 *Spectrum of* $F1_u \rightarrow A0_g^{\pm}$, 1_g, $2_g(^3\Pi_g)$ *transition*

The 46 red degraded bands lying in the region of 380–420 nm are assigned to this new system. These bands are classified into two new subsystems. Details of these subsystems are discussed as follows:

Table 3. Bandhead data of $J0_g^{\pm}\backslash 1_g(^3\Sigma_g^+) \rightarrow D1_u^+(^1\Pi_u)$ transition of Zn_2 molecule.

v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)	v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)
0,0	22548.7	22546.6	5,3	22894.7	22911.4
1,1	22563.5	22567.0	3,0	23016.0	23020.7
2,2	22591.5	22582.3	4,1	23016.0	23032.9
3,3	22612.0	22603.2	0,1	22401.6	22403.7
4,4	22628.8	22626.0	1,2	22423.8	22424.3
5,5	22644.7	22652.2	2,3	22441.4	22446.5
1,0	22701.2	22705.9	0,2	22247.1	22264.5
2,1	22728.6	22721.4	1,3	22290.3	22288.8
3,2	22745.2	22738.3	2,4	22314.2	22315.2
2,0	22856.5	22864.0	3,5	22331.6	22344.1
3,1	22878.4	22877.9	0,3	22130.9	22129.4
4,2	22880.0	22893.3	1,4	22154.4	22156.9

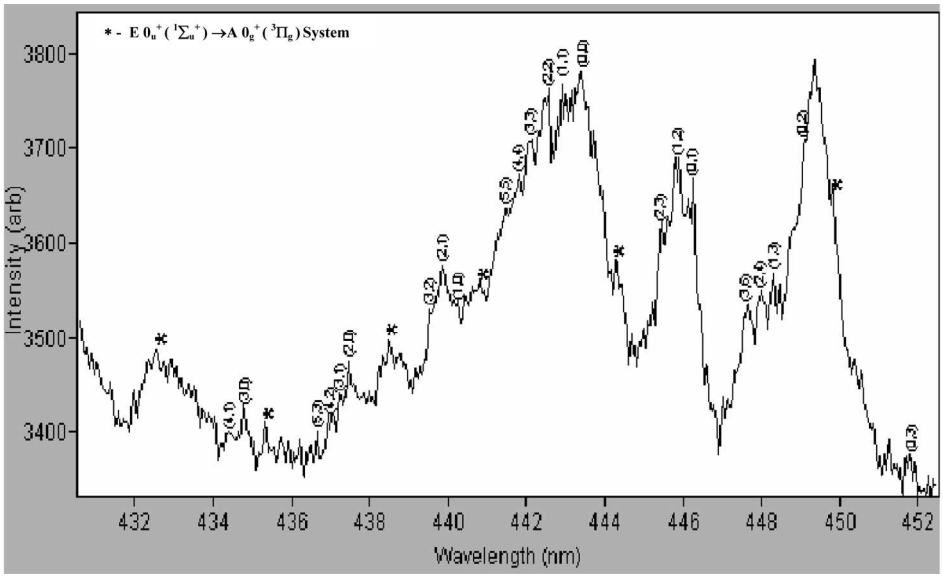

Figure 3. LIBS of $J(^3\Sigma_g^+) \rightarrow D(^1\Pi_u)$ transition of Zn_2 molecule.

3.3.1 *Spectrum of* $F1_u \rightarrow A2_g(^3\Pi_g)$ *transition*

The 30 degraded new bands are classified into $\Delta v = 0$, ± 1, ± 2, ± 3, $+4$, $+5$, $+6$, $+7$, $+8$, $+9$, $+10$, $+11$ and $+12$ sequences of this subsystem. The vibrational constants for A state are very close to the values suggested by Kedziereski *et al* [14]. The bandhead data along with their assignments are presented in table 4. The molecular constants for this subsystem are:

$\nu_{00} = 24770.0\ \text{cm}^{-1}, \quad \omega'_e = 151.6, \quad \omega'_e x'_e = 1.50,$

$\omega''_e = 222.0, \quad \omega''_e x''_e = 1.50.$

3.3.2 *Spectrum of* $F1_u \rightarrow A0_g^{\pm}(^3\Pi_g)$ *transition*

The recorded 16 new red degraded bands are attributed to $\Delta v = 0, \pm1, -2, -3$ and -4 sequences of the subsystem $F1_u \rightarrow A0_g^{\pm}(^3\Pi_g)$. The vibrational constants of this subsystem are the same as reported above for the $F1_u \rightarrow A2_g(^3\Pi_g)$ subsystem. Table 5 is the collection of bandhead data along with their assignments.

Kedziereski *et al* [13] theoretically estimated that the difference of the two components $\Omega = 0_g^{\pm}$ and 2_g of $A(^3\Pi_g)$ state is about 300 cm^{-1} and the same has been observed in the present study. Hence two subsystems may arise due to the transitions between same upper state F and two components of lower state $A0_g^{\pm}$, $2_g(^3\Pi_g)$. The spectrum corresponding to the third component could not be observed. The relative intensity of $F \rightarrow 2_g$ transition is less as compared to $F \rightarrow 0_g^{\pm}$ transition as suggested by Kedziereski *et al* [13]. On the basis of observed transitions $F \rightarrow A2_g(^3\Pi_g)$ and $F \rightarrow A0_g(^3\Pi_g)$ and selection rule $\Delta\Omega = 0, \pm1$, F state may have at least one component as 1_u. T_e value suggests that the new state F lies in between the states $E^1\Sigma_g^+(4\ ^1S + 5\ ^1S)$ and $G^3\Pi_u(4\ ^3D + 4\ ^1S)$ and may arising from $4\ ^3D + 4\ ^1S$.

Hay *et al* [6], Bender *et al* [7] and Couty *et al* [8] have made *ab initio* calculations using SCF-CI method to predict various potential energy curves and states of Zn_2 molecule. It is found that the ground state $X(^1\Sigma_g^+)$ of Zn_2 molecule is repulsive while

Table 4. Bandhead data of $F1_u \rightarrow 2_gA(^3\Pi_g)$ transition of Zn_2 molecule.

v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)	v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)
0,0	24412.0	24412.0	6,1	25046.2	25039.6
1,1	24340.6	24341.6	6,0	25262.0	25258.6
2,2	24290.0	24271.2	7,1	25168.5	25170.2
0,1	24193.4	24193.4	7,0	25391.0	25389.2
1,2	24126.8	24125.6	8,1	25298.5	25297.8
0,2	23962.5	23977.0	8,0	25509.5	25516.8
0,3	23770.2	23764.0	9,1	25420.7	25422.4
1,0	24554.0	24560.6	9,0	25643.0	25641.4
2,0	24705.8	24706.2	10,1	25545.4	25544.0
3,1	24627.3	24629.8	10,0	25768.6	25763.0
3,0	24845.1	24848.8	11,1	25663.42	25662.6
4,1	24775.6	24769.4	11,0	25881.6	25881.6
4,0	24968.0	24988.4	12,1	25832.5	25832.5
5,1	24902.1	24906.0	12,0	25982.2	26000.0
5,0	25118.6	25125.0	13,1	25943.2	25941.8

Table 5. Bandhead data of $F1_u \rightarrow 0_g^{\pm} A(^3\Pi_g)$ transition of Zn_2 molecule.

v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)	v', v''	Wavenumber in cm^{-1} (obs.)	Wavenumber in cm^{-1} (calc.)
0,0	24470.0	24770.0	2,4	24188.7	24206.2
1,1	24697.8	24699.6	0,3	24122.0	24122.0
2,2	24628.4	24629.2	1,4	24050.8	24060.6
0,1	24556.4	24551.0	2,5	24000.5	23999.2
1,2	24471.7	24483.6	3,6	23937.8	23937.8
2,3	24414.3	24416.2	0,4	23914.4	23912.0
0,2	24312.2	24335.0	1,5	24930.6	24918.6
1,3	24263.2	24270.6	1,0	25066.9	25064.2

Table 6. Electronic states of Zn_2 molecule.

Molecular states	Dissociation products	Potential energy/Remarks
$X(^1\Sigma_g^+)$	$4\ ^1S + 4\ ^1S$	Repulsive
$A0_g^{\pm}(^3\Pi_g)$	$4\ ^1S + 4\ ^3P$	2.19 eV/First bound molecular state
$B1_u^+(^3\Sigma_u^+)$	$4\ ^1S + 4\ ^3P$	2.31 eV/More shallow compared to A state
$D1_u(^1\Pi_u)$	$4\ ^1S + 4\ ^1P$	4.13 eV/This state has very small minima
$E0_u^+(^1\Sigma_u^+)$	$5\ ^1S + 4\ ^1S$	5.06 eV/$0_u^{\pm}$, 1_u components
$F1_u$	$4\ ^3D + 4\ ^1S$	5.26 eV; 1_u may be the expected state for F $\rightarrow$ A transition
$G1_g(^1\Pi_g)$	$4\ ^3D + 4\ ^1S$	5.83 eV
$H(^3\Sigma_u^+)$	$4\ ^3P + 4\ ^3P$	6.18 eV
$I(^3\Pi_u)$	$4\ ^3P + 4\ ^3P$	6.61 eV
$J0_g^{\pm}$, $1_g^+(^3\Sigma_g^+)$	$4\ ^3P + 4\ ^3P$	6.92 eV

other electronic states are attractive. Table 6 displays atomic states responsible for these electronic states of Zn_2 molecule along with their dissociation products.

4. Conclusion

In the present study, four new subsystems $E0_u^+(^1\Sigma_u^+) \rightarrow A1_g(^3\Pi_g)$, $F1_u \rightarrow A2_g(^3\Pi_g)$, $F1_u \rightarrow A0_g^{\pm}(^3\Pi_g)$ and $J0_g^{\pm}1_g(^3\Sigma_g^+) \rightarrow D1_u(^1\Pi_u)$ are observed. The (0,0) bands of these subsystems lie at 434.2, 409.5, 403.4 and 443.4 nm. The molecular constants for these subsystems are also determined. The study has also confirmed some electronic states predicted theoretically by Kedziereski *et al* [10,11,13].

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