# SPECTRAL STUDY OF CAESIUM DIMER EXCITED WITH 476.5, 472.7, 465.8 AND 457.9 nm ARGON ION LASER LINES\*

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(Received January 8, 1991)

The results of a study of Cs<sub>2</sub> fluorescence excited by different blue lines of the Ar<sup>+</sup> laser are reported. Special attention was paid to the analysis of the narrow fluorescence band at 522 nm. Approximate assignments of the fluorescence transitions were obtained. The origin of the observed fluorescence is discussed and a rough reconstruction of a fragment of the  $E'(3)^1 \Pi_u$ upper-state potential curve is presented and found to be nearly parallel to the corresponding portion of the ground-state  $X^1 \Sigma_{\mathbf{s}}^+$  potential curve.

PACS numbers: 33.20.Kf

#### 1. Introduction

With atomic mass of 132.9 a.u. caesium forms the heaviest stable alkali diatomic; a loosely bound molecule which under typical experimental conditions in a vacuum cell has several populated vibrational levels and most probable rotational quantum number J exceeding 150. The observed spectra are thus very dense and not easy to interpret. Various experimental techniques, including high resolution methods, were used to obtain spectroscopic information about the Cs<sub>2</sub> molecule. A review of this subject and of the results is given in a work of Amiot, Demtröder and Vidal [1]. Up to now, the structure of several lower lying electronic states has been determined and potential energy curves (or their fragments) found by using RKR and IPA approaches ([1] and references therein). Among these states the ground-state  $X^1 \Sigma_g^+$  is known with great accuracy up to the dissociation limit [2-4].

\*This work was carried out under the Research Project CPBP 01:12.

Most recent studies concern the states, belonging to the group of E states, excited with blue-green light. Two of those, namely  $E(3)^1 \Sigma_u^+$  and  $E'(3)^1 \Pi_u$  (the latter being the highest lying among the known and identified Cs<sub>2</sub> states), have been investigated and partially determined in [1, 5–7]. The use of high resolution Fourier transform spectroscopy and of a number of Ar<sup>+</sup> laser lines for excitation allowed the determination of the potential energy curve of the  $E(3)^1 \Sigma_u^+$  state up to vibrational level v' = 20 [5, 6]. With the same technique Amiot [7] determined the bottom portion of the  $E'(3)^1 \Pi_u$  potential energy curve up to v' = 6. Amiot did not extend the analysis to the higher lying levels (with v' > 6) of the  $E'(3)^1 \Pi_u$  state because of scarce data and of the influence of perturbing states which presumably play a significant role in this spectral region.

A broad absorption band centred at 480 nm has been observed by several authors [8–11]. In the red-wavelength end of this band a narrow satellite at 522.3 nm can be seen. Tellinghuisen and Moeller [12] interpreted the 480 nm band, including the satellite, on the basis of computational simulation of absorption spectra by assuming the existence of an (unknown at that time) single excited-state such that the difference potential (excited-state minus ground-state) reaches a minimum of 19140 cm<sup>-1</sup> at some internuclear distance  $R_n$ . This minimum, of depth equal to the inverse of the satellite central wavelength, was assumed to be the origin of the satellite band.

The narrow band at 522 nm can also be recognized in the fluorescence spectra registered by Katô and Yoshihara [13]. Bieniak, Głódź and Jastrzębski [14] studied the fluorescence and the excitation spectra in the vicinity of the 522 nm region with a broad-band pulsed dye laser tunable in the range 457.2-488.0 nm. The following characteristics of the fluorescence spectra were found:

- position of the band maximum at  $\lambda_{\rm fl} \approx 522$  nm is nearly independent of the exciting light wavelength within the range studied, and the width of the band (FWHM) is ca. 4 nm.
- on the red side of the band ( $\lambda_{fl} > 522 \text{ nm}$ ) fluorescence is very weak for all exciting wavelengths;
- on the blue side of the spectrum ( $\lambda_{\rm fl} < 522$  nm) another fluorescence structure builds up, which develops significantly with lessening energy of excitation photons to finally exceed the intensity of the 522 nm band simultaneously moving away from the  $\lambda_{\rm fl} = 522$  nm band center.

These low resolution spectral investigations have been accompanied by other stages of the study aimed at elucidating the origin and the properties of the 522 nm band and its vicinity. The time dependence of the fluorescence decay was analyzed following excitation with N<sub>2</sub> laser-pumped pulsed dye laser in [15] and following excitation by a mode-locked Ar<sup>+</sup> laser in [17].

The present paper reports investigations of the fluorescence spectra recorded at an increased resolution; which stemmed both from narrower laser bandwidth  $(0.2 \text{ cm}^{-1} \text{ for a single line Ar}^+ \text{ laser against } 10 \text{ cm}^{-1} \text{ for the pulsed dye laser in [14]})$  and from better resolving power of the monochromator used  $(0.3 \text{ cm}^{-1} \text{ against} 25 \text{ cm}^{-1} \text{ in [14]})$ . The use of an Ar<sup>+</sup> laser implied however that the excitation wavelengths were restricted to the lines available with this laser. The analysis of the fluorescence progressions was performed. It supplied an estimate of the energy of excited levels and an approximate assignment of fluorescence transitions. A fragment of the potential energy curve of the electronic state responsible for the fluorescence observed in the region 510–524 nm is approximately reconstructed.

## 2. Experimental

The experimental setup is presented in Fig. 1. Caesium vapour contained in a stainless steel crossed heat-pipe oven was excited by a light beam from the cw multimode Ar<sup>+</sup> laser (2030, Spectra Physics). The laser was consecutively tuned to the lines at 476.5, 472.7, 465.8 and 457.9 nm delivering 2.0, 0.2, 0.5 and 0.9 W respectively. The oven was filled with 5 g of metallic caesium and with 4.4–6 Torr of argon as a buffer gas, and was operated at temperature of  $325-340^{\circ}$ C. The number densities at this temperature are  $\leq 10^{15}$  cm<sup>-3</sup> for dimers and  $\leq 10^{17}$  cm<sup>-3</sup> for atoms.



#### Fig. 1. Experimental arrangement.

The emerging fluorescence was observed at right angle to the incident laser beam with the help of a tuned Czerny-Turner 1 m monochromator (Interactive Technology) whose slit was opened to give spectral resolution from 0.1 to 0.7 Å, depending on the portion of the spectrum registered. Fluorescence photons were registered with the C31034 RCA photomultiplier with GaAs:Cs–O photocathode, cooled down to  $-20^{\circ}$ C. While the monochromator was scanned through the spectral region of interest, the single photon signal, converted into an analogue voltage with Elscint RM-N-1 ratemeter was registered with X–T recorder. Prior to measurements the monochromator was calibrated with neon spectral lines assuring absolute accuracy of wavelength estimation of not worse than 1 Å(ca. 4 cm<sup>-1</sup>). Recorded spectra were digitized for further analysis.

## 3. Results

Fluorescence spectra excited with 476.5, 472.7, 465.8 and 457.9 nm Ar<sup>+</sup> laser lines were registered. The observed wavelengths ranged from the anti-Stokes bands to the long-wavelength end of the 522 nm band except for the vicinity of the laser line. The anti-Stokes lines were used as a source of additional information only and for this reason were not analyzed numerically. Typical spectral resolution was 0.2-0.7 Å, depending on measurement conditions, but some selected fragments of the spectrum were also measured with better resolution, of 0.1 Å. The measurements showed, that the 522 nm band, which was unresolved in [14], has a rich spectral structure. In Figs. 2 and 3 fragments of the fluorescence spectra, in the vicinity of the 522 nm band, and excited by different laser lines are shown. Because excitation of Cs<sub>2</sub> with the 457.9 nm laser line is reported here for the first time in the literature, the remaining part of the fluorescence spectrum for that laser wavelength is also shown in Fig. 4. The essential characteristics of the recorded spectra will now be described and will be followed by a discussion of the numerical processing of the data and of the results.

## 3.1. Description of spectra

#### 3.1.1. Spectrum excited with the 457.9 nm line

In the Stokes spectrum (see Fig. 4 and Fig. 2(a) bands closest to the excitation wavelength are separated by about 41 cm<sup>-1</sup>, which corresponds to distances between the lowest vibrational levels of the ground-state  $X^1 \Sigma_g^+$  the most probable rotational quantum number J'' = 150, namely:  $T(v'' = 1, J'' = 150) - T(v'' = 0, J'' = 150) = 41.3 \text{ cm}^{-1}$ , where T(v, J) denotes the term value. In the region 463.9–518 nm one progression with irregular line intensities dominates, in some fragments of the spectrum every second line is missing. On the red side of the spectrum a very strong 522 nm band can be seen which is accompanied by a much weaker but still distinct 519 nm band.

In the anti-Stokes spectrum there are 14 quite regular bands (with barely resolved structure) which gradually weaken towards shorter wavelengths. The first three of these bands are by far the most intense. The number of the observed anti-Stokes bands indicates, that the absorption from up to 14 lowest vibrational levels of the  $X^1\Sigma_{\mathbf{r}}^+$  state takes place. Consequently the spacings between the first



Fig. 2. Fluorescence spectra of  $Cs_2$  excited with different  $Ar^+$  laser wavelengths and observed in the range 507-525 nm. Excitation wavelengths: (a) 457.9 nm, (b) 465.8 nm (this spectrum is cut off at 522 nm because intensity exceeds the range set, in Fig. 3 the entire 522 nm band is recorded with higher resolution), (c) 472.7 nm, (d) 476.5 nm. Vertical scales are in arbitrary units which vary for each spectrum.



Fig. 3. The fluorescence band at 522 nm excited with 465.8 nm laser line. This spectrum (note the higher resolution) relates to the one in Fig. 2(b).



Fig. 4. Fluorescence spectrum of  $Cs_2$  excited with 457.9 nm line registered beginning from the first Stokes bands. This spectrum is continued in Fig. 2(a). The same scales are maintained.

Stokes bands should amount to  $T(v'' = 15, J'' = 150) - T(v'' = 14, J'' = 150) = 38.8 \text{ cm}^{-1}$ .

The separations between the strongest Stokes lines show however, that the absorption takes place from the lowest vibrational levels (up to v'' = 4). Several weak series with distances of about 38.5 cm<sup>-1</sup> between the first Stokes lines can also be seen. This leads to the conclusion that with the 457.9 nm excitation the strongest fluorescence progressions are related to absorption from the lowest ( $v'' = 0 \div 4$ ) vibrational levels while the weaker ones, to absorption from higher levels (up to v'' = 14).

#### 3.1.2. Spectrum excited with the 465.8 nm line

The pattern of Stokes spectrum is quite complicated because apparently more than one strong progression is excited with this laser line. The intensity of the lines varies very slowly in the region between the laser line and  $\lambda_{\rm fl} = 521.7$  nm, and then grows rapidly developing the strong 522 nm band (see Fig. 2b and Fig. 3). The latter consists of more then 10 distinct progressions.

The anti-Stokes spectrum reveals 9 bands with gradually decreasing intensityindicating that absorption takes place from the lowest 9 vibrational levels.

# 3.1.3. Spectrum excited with the 472.7 nm line

The Stokes spectrum excited with the 472.7 nm line is very complex. The first Stokes bands are accompanied by strong satellites related to P and R branches of the fluorescence progressions following R and P excitation respectively. This points to significant contribution of the P, R transitions to the whole fluorescence. Except for the first Stokes bands the pattern of the spectrum becomes very irregular. Two strong bands of comparable intensity are seen at 519 nm and at 522 nm (Fig. 2c).

In the anti-Stokes region 7 bands are observed, but only the first is strong, which indicates that the strongest absorption may occur from the  $v^{"}=0$  and 1 levels.

## 3.1.4. Spectrum excited with the 476.5 nm line

In the Stokes spectrum there is one dominant progression of very irregular intensity which is accompanied by many weaker series. Of the two bands formerly observed in the spectrum excited by the 472.7 nm line, the one at 522 nm is still distinct but much weaker than the band at 515 nm which is displaced from 519 nm for 472.7 nm excitation.

The anti-Stokes spectrum reveals 11 gradually weakening bands. The longest progressions in the spectrum excited by this wavelength have been identified and assigned by Amiot [7] as originating in  $E'(3)^1 \Pi_{\rm u} \rightarrow X^1 \Sigma_{\rm g}^+$  transition. By comparing the data of Amiot with our spectrum we were able to establish that the strongest progression is connected with transition  $(v' = 13, J' = 160) \rightarrow (v'', J'' = 160)$ , with v'' = 0 being the initial level from which excitation takes place.

#### 3.2. Analysis of the spectra

The aim of our study was to determine the origin of the band observed at

522 nm and of the spectrum in its vicinity. The fluorescence consists of a superposition of progressions of lines originating from transitions from the initially populated upper levels (v', J') down to the various ground-state levels (v'', J''), in accordance with the rotational selection rules and Franck-Condon factors. Each progression consists of lines corresponding to fluorescence connecting one excited rovibrational level (v', J') with sequence of ground-state levels:

$$(v', J') \to (v'', J''), (v''+1, J''), (v''+2, J'')...$$
 (1)

with

$$J'' - J' = 0, \pm 1$$

Analysis carried out on this basis allowed, within the estimated uncertainty limits, to reach an assignment of the ground-state level from which the excitation originates and of the energy of the upper-state for each identified progression.

# 3.2.1. Computational procedure and results

The position of each recognizable spectral line and some additional information such as intensity were recorded. The measured line positions were then converted to wavenumbers. Further data analysis was adapted to the overall accuracy of the wavenumber determination and to the spectral resolution, both being relatively low when compared to measurements in Ref. [7]. For fitting some distinct progressions of lines with regular distances were selected from the variety of lines excited by a single laser wavelength. The analysis of the experimental data was carried out by the computer program (including a least squares minimizing procedure) using precisely determined Dunham coefficients for the ground electronic state [3] and taking the energies of the ground-state levels (v'', J'') states to be given by the Dunham expansion in (v''+1/2) and J''(J''+1). The adjustable parameters were  $v_1''$  and J'' with  $(v_1'', J_1'')$  denoting the lower level of the transition corresponding to the first observed line in the progression. Another fitted parameter was the term value T' of the excited-state level. The formula used in the computation was of the form:

$$\sum_{i} (E_{\rm obs}^{(i)} - E_{\rm comp}^{(i)})^2 = \min,$$
(2)

with

$$E_{\rm comp}^{(i)} = T' - T''(v_1'' + i - 1, J_1''),$$

where  $E_{obs}^{(i)}$ ,  $E_{comp}^{(i)}$  denote wavenumbers of the *i*-th observed computed line of the progression,  $E_{comp}^{(i)}$  being computed with the known molecular coefficients and the fitted T',  $v''_1$ ,  $J''_1$  values and the summation runs over all lines belonging to it (i = 1, 2, 3...), T'' denotes the term value of the ground-state level.

With the known wavenumber of the laser line  $E^{(las)}$  and the fitted  $v_1''$ ,  $J_1''$  values, the ground-state level pumped by the laser  $(v_0'', J_0'')$  can be found from

$$T''(v_0'', J_0'') = T''(v_1'', J_1'') + E_{obs}^{(1)} - E^{(las)}$$
(3)

with  $J_0'' - J_1'' = 0, \pm 2$  depending on the branch.

Owing to spectral resolution of the experiment, it was not possible to reach a unique assignment with the procedure described by Eqs. (2) and (3) and for this reason the final assignment was decided on the basis of additional criteria such as inspection of anti-Stokes bands. Alternatively a mean value of the most probable parameter values was taken with uncertainty limits extending from the maximum to the minimum value. Tables I and II present for each progression the derived assignments  $v_0''$ ,  $J_0''$  of the lower levels from which the excitation takes place. Also the range of v'' included in the analysis of a given progression and the excited level term value T' are presented. The estimated uncertainty is given for all values. For some well determined progressions, the assignment of the branch type (P, Q or R) appeared to be reliable. In more questionable cases the type is not given.

In Table I the strong progressions which develop in the region of the first Stokes bands are compiled. Each progression was followed down to the end of recorded spectrum (for some spectra) or to the range where resolution and/or Franck-Condon effects prevented further recognition of the series.

The content of this table can be compared with that of Table I of [7] where precise identification of several transitions observed on excitation with Ar<sup>+</sup> laser lines ranging from 501.7 nm to 465.8 nm is given. A satisfactory agreement with [7] for the same exciting laser lines is found, in that the progressions analyzed in Ref. [7] can be recognised in Table I. For the 476.5 nm laser line the progressions found by Amiot were re-identified and traced down in the recorded spectra and therefore the exact values taken from [7] are given in that part of Table I. The numbering of the progressions (the first column of the table) is a remnant of the data analysis stage and is for reference purposes only. The lower case letters denote progressions found in the analysis of the spectra recorded at higher resolution but constrained to only a few ( $\leq 10$ ) Stokes bands. The capital letters denote the series found in the spectra recorded with a slightly lower resolution but covering the spectral range from the laser line up to the green bands. In some cases it can be seen for given laser line that the corresponding lower and upper case letters denote the same progressions, e.g. the series a/A, b/B, c/C for 472.7 nm line or a/A, b/B for 465.8 nm line. The reliability of the assignments can be checked to some extent by comparison of the relevant parameter values. For other cases no simple correspondence exists and it is also possible that different series may be seen in each subgroup.

Further analysis was aimed at revealing the origin of the observed strong green fluorescence. For this purpose the progressions constituting a significant part of the 522 nm fluorescence band and of its vicinity were identified and assigned. Table II summarizes the results. The series are denoted by lower case letters for reference purpose only, there is no intentional correlation with data of Table I.

It is to be noted that the series compiled in Table I and Table II were identified independently. Due to the complexity of the spectra it was not possible to trace the single progression through the whole spectral range with any confidence. Only for the 476.5 nm laser line we were able to follow the consecutive lines for the series taken from [7] with reasonable reliability up to the green spectral region. The results presented in Table II are less trustworthy than these in Table I

# TABLE I

Some approximately identified fluorescence series excited in Cs<sub>2</sub> by different Ar<sup>+</sup> laser lines and recognized in the region of first Stokes bands. The first column contains numbering of progressions in small or capital letters for each laser line (for explanation see text). The second column gives the energy of the excited-state level T' in respect to the minimum of the ground-state potential. The third column gives the range of levels  $\bar{v}''$ covered by the observed lines ( $\Delta v''$ ). The fourth and the fifth columns present the rotational ( $J_0''$ ) and vibrational ( $v_0''$ ) assignments of the ground-state level being pumped. The last column gives the probable type of the transition. For the 476.5 nm line all values are exact and taken from Ref. [7].

	T'	$\Delta v''$	$J_0''$	$v_0''$	branch		
laser line 476.5 nm							
a	21076	1941	77	0	R		
Ь	21080	19-41	81	0	Q		
с	21194	19-43	113	1	R		
d	21272	15-46	126	2	Р		
е	21195	6-43	128	0	Q		
f	21302	1-47	160	0	Q		
g	21410	2-59	187	0	Q		
h	21690	24-51	244	0	Р		
i	21690	2451	244	0	R		
lase	r line 472.7 ni	n					
a	21288(40)	2-8(1)	98(50)	0(1)	Q		
b	21961(40)	2-8(1)	254(15)	1(1)	Q		
с	21529(40)	2-8(1)	166(20)	1(1)	P		
d	21532(40)	2-8(1)	177(25)	0(1)	P		
e	21504(40)	2-8(1)	170(25)	0(1)	P -		
f	21588(40)	2-8(1)	186(25)	0(1)	R		
g	21502(80)	5-9(2)	156(70)	1(2)	Q		
ĥ	21584(40)	2-8(1)	187(25)	0(1)	Q		
i	21532(80)	4-8(2)	164(50)	1(2)	Q		
A	21294(40)	4-16(1)	100(50)	0(1)	Q		
В	21963(40)	2-22(1)	254(25)	1(1)	Q		
С	21516(40)	2~10(1)	162(25)	1(1)	P		
$\mathbf{F}$	21636(40)	4-20(1)	197(25)	0(1)	R		
G	21475(80)	5-19(2)	148(55)	1(2)	Q		
Ι	21463(80)	5-25(2)	132(70)	2(2)	Q		
J	21883(40)	8-24(1)	240(15)	1(1)	Q		
Κ	21338(40)	7-21(1)	118(60)	0(1)	ġ		
Μ	21584(40)	6-26(1)	176(20)	1(1)	Q		
laser line 465.8 nm							
a	21943(130)	5-9(4)	168(130)	3(4)	Q		
b	21633(40)	3-7(1)	93(50)	1(1)	Q		
e	22020(80)	4-7(2)	205(40)	1(2)	Q		

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TABLE I (cont.)

	T'	$\Delta v''$	$J_0''$	$v_0''$	branch
$\mathbf{A}$	21971(130)	9-43(4)	175(80)	3(4)	Q
В	21665(45)	12 - 34(1)	106(30)	1(1)	$\bar{Q}$
$\mathbf{E}$	21993(130)	14-32(4)	170(100)	4(4)	Q
F	22070(100)	17-35(4)	192(50)	4(4)	$\dot{P}$
G	21739(70)	17 - 27(2)	133(60)	1(2)	Q
H	21584(35)	17 - 27(1)	65(40)	1(1)	?
J	21574(30)	28-46(1)	79(50)	0(1)	R
laser line 457.9 nm					
A	22131(80)	13-77(3)	114(70)	3(3)	Q

because (i) the identified progressions were shorter and (ii) the displacements of the studied lines from the laser line were greater, leading to larger uncertainties on extrapolation and thus in the derived assignments.

## 3.2.2. The upper state for green fluorescence

It follows from the results given in Table II that the absorption, which leads to fluorescence observed in the green spectral region, i.e. in the 522 nm band and in its vicinity, originates in the few lowest vibrational levels of the ground-state  $X^1\Sigma_{g}^+$  and fluorescence transitions terminate on highly excited levels of that state (v'' in the range ca. 50-90 depending on the laser wavelength). The term values T' show that the upper (excited-state) levels populated in the act of absorption are situated in an energy region above the known part of the  $E'(3)^1 \Pi_{\rm u}$  potential (see Figs.5 and 6). For both excited-states E and E' the equilibrium internuclear distances are greater than in the ground-state  $X^1\Sigma_g^+$ . Even if a priori identification of the upper state active in the analyzed fluorescence is avoided it seems reasonable to assume that the same is true for this state. Within a simplified approach of the classical Franck-Condon principle one can thus infer that excitation leads to the vicinity of the classical turning point on the repulsive branch of the excited-state potential curve, and the strong green fluorescence occurs between the turning points on the attractive branches of both excited- and ground-state potential energy curves. We assume that the strongest emission line (corresponding to maximum of the overlap integral) in the green part of each progression connects the outer turning points of both potentials [16]. From the analysis of progression the vibrational level on which the strongest line terminates can be determined. With the known ground-state potential curve [1, 3] the internuclear distance  $R_n$  of the outer turning point related to this level was evaluated. To reconstruct the shape of the excited-state (rotationless) potential curve, the observed wavenumbers of the strongest lines were corrected for the contribution from molecular rotation. Rotational energy of the ground-state level can be computed with the known molecular constants. In order to correct the term value T' it was assumed that rotational energy of the upper level can be approximated using the molecular constants for

# TABLE II

Some approximately identified fluorescence series excited in  $Cs_2$  with different  $Ar^+$  laser lines and recognized in the region of the 522 nm band. The description of the columns is the same as in Table I. Generally the series found are very short and the distance to the laser line is rather big, therefore, the systematic uncertainties are supposed to be greater than in Table I.

	<u>T'</u>	$\Delta n''$		<i>n</i> <sup>//</sup>	branch		
laser line 476 5 nm							
2	22001(40)	55-60(4)	269(45)	4(4)	?		
ъ	21871(40)	54-59(4)	246(45)	4(4)	?		
~ ~ ·	21509(100)	52-56(4)	168(60)	4(4)	?		
ď	21000(100) 21932(55)	54-58(4)	258(45)	4(4)	?		
Ā	21720(70)	54-58(4)	215(45)	4(4)	?		
f	21643(90)	54-57(4)	203(45)	4(4)	?		
lase	laser line: 472.7 nm						
a	21280(30)	48-55(1)	89(40)	0(1)	R		
Ъ	21477(80)	50-58(3)	150(80)	1(3)	Р		
d	21547(80)	54-59(3)	156(70)	2(3)	Q		
е	21913(70)	52-57(3)	237(35)	2(3)	Q		
f	21808(70)	57-62(3)	216(40)	2(3)	R		
g	21912(50)	59-62(3)	237(30)	2(3)	Q		
m	22026(50)	57-61(3)	258(30)	2(3)	Q		
р	21579(80)	54-58(3)	164(40)	2(3)	?		
q	21551(80)	53-57(3)	154(70)	2(3)	R		
r	21444(80)	52-56(3)	123(75)	2(3)	?		
s	21493(75)	51-57(3)	143(85)	2(3)	Р		
lase	r line 465.8 n	m			·		
a	21968(65)	70-74(3)	174(55)	3(3)	Q		
Ъ	21860(65)	68-73(3)	141(75)	3(3)	R		
с	21944(65)	68-72(3)	180(55)	2(3)	?		
d	21863(65)	67-72(3)	145(75)	3(3)	?		
е	21927(40)	67-71(2)	187(30)	1(2)			
k	22142(40)	69-72(2)	233(30)	1(2)	?		
m	21914(40)	68-71(2)	184(40)	1(2)	P		
q	22108(65)	70-73(3)	217(40)	2(3)	?		
u	21858(65)	68-71(3)	159(65)	2(3)			
x	21837(100)	70-74(4)	122(90)	4(4)	?		
у	21958(65)	7.0-74(3)	172(40)	3(3)	?		
laser line 457.9 nm							
a	22105(40)	82-85(2)	112(60)	2(2)	?		
Ъ	22283(55)	83-88(3)	159(55)	3(3)	?		
C	22014(40)	76-80(2)	119(55)	0(2)	?		
d	22487(60)	78-88(4)	225(45)	1(4)	?		

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Fig. 5. Potential energy curves of the Cs<sub>2</sub> molecule relevant to present work. The  $X^1 \Sigma_g^+$ ,  $E(3)^1 \Sigma_u^+$  and  $E'(3)^1 \Pi_u$  potentials are calculated with coefficients taken from Refs. [3], [1] and [7] respectively. The points (determined in the procedure discussed in the text) follow the shape of that fragment of excited-state potential which is responsible for the fluorescence in the 522 nm band and in its vicinity. The full circles and the triangles come from an analysis of fluorescence excited with 476.5 nm; the squares with 472.7 nm; the rhombi with 465.8z nm; and the stars with 457.9 nm laser line. The dotted line serves to guide an eye only. The dashed curve represents a fragment of the ground-state potential shifted upwards by 19220 cm<sup>-1</sup> (see text). The typical uncertainties are depicted.

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Fig. 6. A blowup of inset region of Fig.5.

the known part of  $E'(3)^1 \Pi_u$  state found in Ref. [7]. This simplifying assumption has only a minor effect on the accuracy of our analysis since rotational constants show rather weak changes for the known excited electronic states of Cs<sub>2</sub>.

As a result of the procedure applied to progressions shown in Table II as well as to those excited by 476.5 nm and shown in Table I, the points approximating outer turning points of the upper state potential were obtained. These points approximate the shape of potential curve of the state responsible for the observed fluorescence. The reconstructed fragment of the potential is shown in Fig. 5. The uncertainty of the experimental points depends on (i) assignment accuracy of  $v''_0$ and (ii) accuracy of determination of the strongest line in the series as owing to overlap of several progressions it is possible to mistake a superposition of some neighbouring lines as the single strongest line. The resulting typical errors are depicted in Fig. 6 for two experimental points.

## 4. Discussion

It follows from the analysis of the results of [7] that the strong bands observed at 515-519 nm in the spectra excited by 472.7 and 476.5 nm laser lines belongs to the  $E'(3)^1 \Pi_u \to X^1 \Sigma_g^+$  transition. At least this is evident for fluorescence pro-

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gressions observed both in this work (see Fig. 2(c, d)) and in Amiot's experiment. Many progressions observed by Amiot were identified in our spectra. The analysis of the series excited by the 476.5 nm laser line (see Table I) with the procedure discussed here lead to the points marked by full circles in Fig. 5. Other depicted points correspond to the series compiled in Table II and relate to the portion of the excited-state potential responsible for formation of the 522 nm band.

All points, determined with the help of the procedure described in the preceding section, seem to be spread along the same line (see Fig. 5). The accuracy of the applied method does not allow for determination of the exact shape of the potential energy curve of the upper state. The plotted dotted line serves only as a visual guide symbolizing such potential. It constitutes, however, a rather natural extension of the  $E'(3)^1 \Pi_u$  state potential. Thus in view of presented data it seems unnecessary to postulate the existence of any other excited-state (apart from  $E'(3)^{1}\Pi_{u}$  in order to explain the origin of the 522 nm band and its strong side band. The only difference between both bands is that the 522 nm band originates in the higher lying levels of the E' state than the accompanying fluorescence, namely in the energy region where the potential curve of the E' state becomes almost parallel to the ground-state potential. One can also infer that the absorption of the exciting light leading to the 522 nm band occurs in the higher lying levels of the ground-state. In fact the resulting decrease of intensity of the 522 nm band with the increasing wavelength of the exciting laser was observed in the experiment. It is to be noted that the results of this work confirm some of our earlier conjectures on the origin of the observed fluorescence bands [14].

In [12] the authors have established the energy difference between the relevant regions of the postulated excited-state and the ground-state potentials to be  $\approx 19140 \text{ cm}^{-1}$ . Our results show that the segments of the potential curves of both states which are active in creating the 522 nm band are almost parallel to each other and separated by ca. 19220 cm<sup>-1</sup> (see Fig. 5 where the dashed curve represents a portion of the ground-state potential shifted upwards by 19220 cm<sup>-1</sup>). The discrepancy between both numbers can be explained as follows. In [13] the "effective" potential averaged over thermal distribution of rotational states was determined, in contrast with the present results in which the experimental points and the curves of Fig. 5 follow the "rotationless" potential curves. The difference is well fitted by the energy correction evaluated for mean rotational number of the levels relevant for the analysis.

The manifestations of perturbations reported in Ref. [7] and indirectly through lifetime measurements in Ref. [17] indicate that in more precise analysis the involvement of another electronic state or states has to be accounted for. In Ref. [17] decay of Cs<sub>2</sub> fluorescence excited at 476.5 nm and observed at several wavelengths in green spectral region was found to consist of three exponential components with lifetimes  $\tau_1 = 29$  ns,  $\tau_2 = 4.5$  ns and  $\tau_3 \leq 1$  ns respectively. The fluorescence was interpreted as originating from the  $E'(3)^1 \Pi_u$  state perturbed by the bound  $(3)^3 \Pi_u$ state and the repulsive  $(3)^3 \Sigma_u$  state.

Further study using the higher time- and/or spectral-resolution technique could shed more light on the role of perturbing states in this spectral region.

#### Acknowledgments

The DFG Sonderforschungsbereich 91 is gratefully acknowledged for supporting the experimental part of this work. One of us (BB) is greatly indebted to Prof. Dr. W. Demtröder who invited him to perform this experiment in his laboratory in the University of Kaiserslautern and whose experience was of great help. Many thanks are also due to Prof. Dr. K. Rosiński and to Dr. M. Głódź for numerous discussions.

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