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Absorption measurements in dense cesium vapor using a UV–violet light-emitting diode

T. Ban[1], **H. Skenderović**[1], **S. Ter-Avetisyan**[2], **G. Pichler**[1]

[1] Institute of Physics, P.O. Box 304, 10000 Zagreb, Croatia
[2] Institute for Physical Research, Armenian Academy of Science, Ashtarak-2, 378410 Armenia

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Abstract. We present results of absorption measurements in a dense superheated cesium vapor generated in an all-sapphire cell using a UV–violet light-emitting diode as a continuum source. Due to the very effective thermal destruction of Cs_2 molecules, a number of diffuse and satellite bands appear around higher members of cesium principal series lines, which are not easily visible in saturated cesium vapor. From the temperature dependence of the diffuse features we can distinguish short-range singlet transitions from temperature-independent spectral features that stem either from a shallow lowest triplet state or from the long-range photo association spectra of triplet or singlet Cs_2 molecules. The limits of the present interpretation of the observed bands in the UV–violet spectral region are discussed.

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Simple absorption measurements are among the most powerful quantitative determinations in physics, provided the light continuum or laser light source intensity do not cause any saturation effects, and the sample has a relatively small optical thickness. When a monochromator is used for spectrally resolved absorption measurements, it is desirable that the light source emits a narrow-band continuum in order to avoid stray light from other spectral regions of the white-light source. A very stable and narrow-band continuum light source is a light-emitting diode (LED). Beside super-bright red LEDs, recently there are several super-bright LEDs in the blue (NSPB500 S) and green (NSPG500 S) spectral regions from NICHIA (Japan) (http://www.nichia.com). Prior to these devices, NICHIA's first blue LED production offered a blue LED peaking at about 450 nm (NLPB500). At higher electric currents through the LED an additional ultraviolet spectral component peaking at about 386 nm appears [1]. When the electric current through the diode increases up to 100 mA, the intensity of the 386 nm component surpasses five times the intensity of the 447 nm component. In Fig. 1 we present the spectra of a NLPB500 blue LED for the currents of 30 mA and 100 mA. At 100 mA we have a continuum light source with two maxima at 391 nm and at 450 nm, with half widths of about 12 nm and 95 nm, respectively. We used this continuum source for the absorption measurements in dense cesium vapor generated in the all-sapphire cell [2]. In the spectral region between 380 and 440 nm the halogen–tungsten lamp is very weak, which decreases the signal-to-noise ratio. Therefore the use of a NLPB500 blue LED becomes essential for accurate absorption coefficient measurements in the near ultraviolet spectral region. In this spectral region we find the third cesium principal series doublet ($6s_{1/2} \to 8p_{3/2,1/2}$ at 387.61 and 388.86 nm) with the corresponding satellite bands [3]. The Cs principal series lines $6s_{1/2} \to np_J$ were experimentally investigated by Heinke et al. [4], who investigated the self-broadening of the Cs np_J levels in the very far quasistatic wings and observed pronounced satellite bands in the blue wings of the $6s_{1/2} \to np_J$ lines ($n = 8, 9, ..., 23$). These satellite bands usually arise because of the extrema in the relevant difference-potential curves. If these extrema are located at large interatomic distances (long-range region) where the lower-potential curve is essentially a horizontal straight line, then the difference-potential curves become equal to the corresponding upper-interaction potential curves. It was found that the system of satellite bands around principal series lines approaches the centers of the lines with increasing n. For the third Cs principal series doublet $6s_{1/2} \to 8p_{3/2,1/2}$ the positions of the maxima of the satellite bands were approximately at 387.4 and 386.9 nm [5].

In the present work we shall show how the superheating of cesium vapor can lead to the appearance of a few new spectral features in the wavelength region from 380 to 410 nm. Their attribution to singlet Cs_2 ($X\,^1\Sigma_g{}^+$) molecules or triplet Cs_2 ($a\,^3\Sigma_u{}^+$) will be discussed.

1 Experiments

The experiments have been performed using a simple absorption setup. The main part is the oven with a sealed-off cylindrical all-sapphire cell (ASC), 16 cm in length, containing pure cesium (with small traces of potassium and rubidium). The detailed description of the ASC is presented in [6, 7].

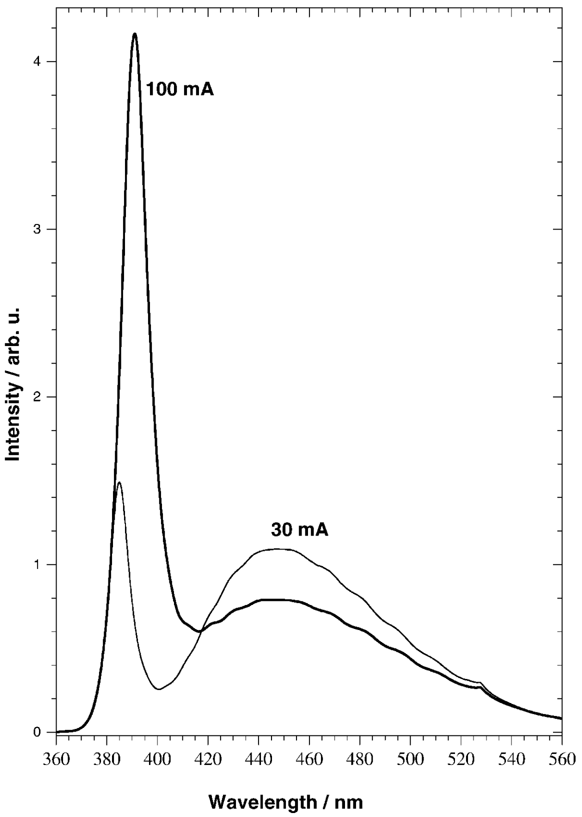

Fig. 1. Spectra of a NLPB500 blue LED for currents through the LED of 30 mA and 100 mA

The temperature of the cesium vapor inside the ASC was approximately determined by a thermocouple positioned at the middle of the outside wall of the ASC.

During the initial heating, saturated cesium vapor appears in the ASC. The vapor is in thermal equilibrium with liquid cesium, and consists of cesium atoms and a few percent of cesium molecules. It was found by absorption measurements that the maximum density of the saturated vapor corresponds to the vapor temperature of $T_0 = 424\,°\mathrm{C}$ ($N_{\mathrm{Cs}} = 3.5 \times 10^{17}\,\mathrm{cm}^{-3}$ [8]). At that temperature all metallic cesium in the ASC evaporates and the cesium dimer density reached its maximum value. At the higher temperatures the cesium molecular absorption decreased due to thermal dissociation of cesium dimers. Above 424 °C the cesium atom number density stays essentially constant (it actually slightly increases because of dimer reduction).

The ASC was irradiated by the continuous light from a NLPB500 blue LED, which gives at 25 °C the optical output power of 3 mW at a DC voltage of 5 V and a DC forward current of 20 mA. At these temperature and current conditions the NLPB500 blue LED has a typical luminous intensity of 2 cd. At a forward current of 100 mA the second pronounced peak at about 390 nm appears, which is used for the near-UV absorption measurements in saturated cesium vapor.

The NLPB500 blue LED light passing the absorption cell was analyzed using a 'Jobin Yvon THR' 1.5-m grating spectrometer equipped with a Hamamatsu R936 photomultiplier. The output signal was fed into a SR510 lock-in amplifier and stored in a laboratory PC. The absorption spectrum was scanned by rotating the holographic grating (1200 grooves/mm) with a computer-controlled stepper motor. The resolution of the system was 0.035 nm with 20-μm slit widths.

2 Results

The absorption spectrum of cesium vapor in the wavelength range from 380 nm to 450 nm was measured for the temperature range up to 700 °C. In Fig. 2 we show the transmission curves at 424 °C, 490 °C, 560 °C and 695 °C in the wavelength region from 376 nm to 450 nm, using the LED a 100-mA forward electric current. In the spectrum at the lowest temperature only the second and third principal series of the Cs doublets ($6s_{1/2} \rightarrow 7p_{3/2,1/2}$ at 455.53 nm and

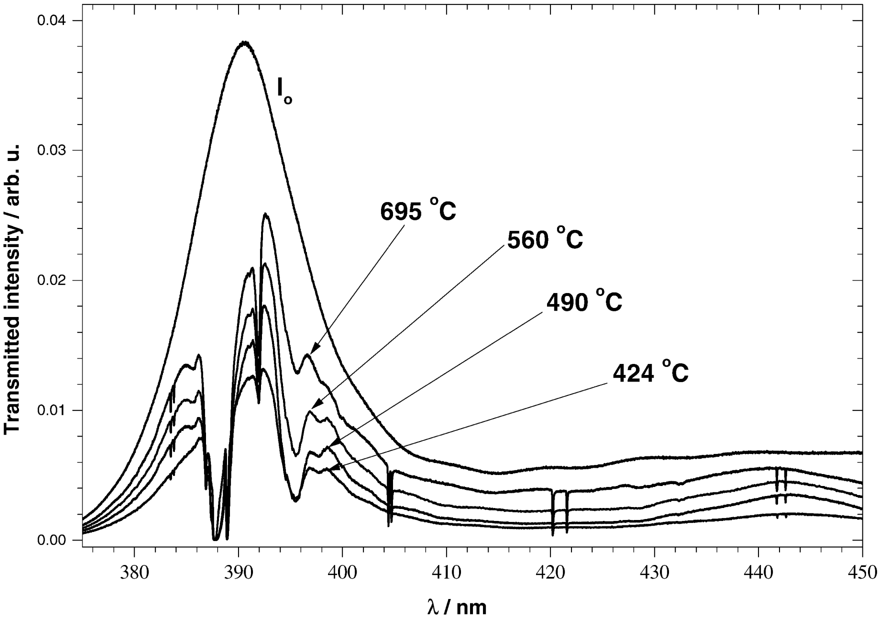

Fig. 2. Transmission spectra of dense cesium vapor for 424 °C, 490 °C, 560 °C and 695 °C in the wavelength range from 375 nm to 450 nm, using a NLPB500 blue LED with a 100-mA forward electric current

459.32 nm, $6s_{1/2} \rightarrow 8p_{3/2,1/2}$ at 387.61 and 388.86 nm) are present. At the higher temperatures, besides these allowed transitions the forbidden atomic transitions $6s_{1/2} \rightarrow 7d_{5/2,3/2}$ (383.49 nm, 383.8 nm) and $6s_{1/2} \rightarrow 6d_{5/2,3/2}$ (441.73 nm, 442.76 nm) can be seen, new cesium satellite bands and Cs_2 molecular features appear in the spectrum. In the spectra above 424 °C the molecular absorption gradually decreases, which is a consequence of increasing thermal dissociation of Cs_2 molecules. In the wavelength region presented in Fig. 2, the molecular absorptions are dominated by molecular states with atomic asymptotes $6s+7s$, $6s+7p$, $6s+7d$. In all absorption spectra, the second principal series doublets of K ($4s_{1/2} \rightarrow 5p_{3/2,1/2}$ at 404.41 nm, 404.72 nm) and Rb ($5s_{1/2} \rightarrow 6p_{3/2,1/2}$ at 420.18 nm, 421.55 nm) impurities can also be recognized.

The cesium transmission spectrum is transformed into the absorption-coefficient spectrum of Fig. 3 by means of the Beer–Lambert law [9]. Besides the atomic Cs lines (allowed and forbidden) and K doublet lines, there are several satellite bands peaking at 385.79 nm, 386.89 nm, 387.42 nm, 391.95 nm, 395.4 nm and 397.7 nm, which will be further discussed concerning their temperature behavior above 424 °C. The 385.5-nm, 386.9-nm and 387.4-nm satellite bands in the blue wing of the Cs $6s_{1/2} - 8p_{3/2}$ atomic line exhibit no temperature dependence in the $(424-700)$ °C interval. The absorption coefficient of the satellite band peaking at 391.9 nm in the red wing of the Cs $6s_{1/2} - 8p_{1/2}$ atomic line is also temperature-independent. These satellite bands, with no temperature dependence beyond 424 °C, are entirely due to the following photo-association process:

$$\mathrm{Cs}(6s) + \mathrm{Cs}(6s) + h\nu \rightarrow \mathrm{Cs_2}^* , \tag{1}$$

where Cs_2^* denotes the highly excited cesium dimer. The nascent Cs_2^* dimers are subjected to strong collisional processes, which lead to collisional stabilization within Cs_2^* dimers. However, they are predominantly collisionally dissociated at high cell temperatures, especially if the dissociation energy of the excited states is smaller than the dissociation energy of the ground state.

Two molecular bands, one peaking at 395.4 nm, and the other peaking at 397.7 nm, show a very interesting temperature dependence typical for the Cs_2 $1(X)\,^1\Sigma_g{}^+$ ground electronic state. We observed for the molecular band peaking at 395.4 nm a steady rise of the absorption coefficients up to 424 °C, and beyond this critical temperature there is an exponential decrease. We interpret such a behavior as a consequence of thermal destruction of Cs_2 molecules at temperatures higher than 424 °C. Indeed, the absorption coefficient of these molecular bands is proportional to the square of the particle density N and an exponential Boltzmann factor involving the temperature T of the vapor:

$$k \propto N^2 \exp -\{[U(R) - U(\infty)]/k_\mathrm{B}T\} , \tag{2}$$

where $U(R)$ is the molecular potential of the lower state at internuclear distance R. Since the total number density of cesium atoms effectively does not change, we can consider N^2 as a constant factor. However, $[U(R) - U(\infty)]$ can be effectively considered as D_0, the dissociation energy of the Cs_2 molecule. In Fig. 4, the k values for the Cs_2 bands at 395.4 nm and 422.5 nm are plotted as a function of the inverse temperature, in the interval between 455 °C and 700 °C. From the slopes of the obtained straight lines we estimated the singlet ground-state dissociation energy. Obtained values of $(3460 \pm 80)\,\mathrm{cm}^{-1}$ and $(3700 \pm 150)\,\mathrm{cm}^{-1}$ are close to the values $(3648 \pm 0.8)\,\mathrm{cm}^{-1}$ [10] and $3646\,\mathrm{cm}^{-1}$ [11] obtained from careful analysis of the Cs_2 molecular bands. The second peak at 397.7 nm exhibits a similar temperature dependence. According to this, it can be concluded that the Cs_2 molecular bands peaking at 395.4 nm and 397.7 nm belong to the absorption from the Cs_2 $X\,^1\Sigma_g{}^+$ state to excited Cs_2 singlet state(s) which are connected with atomic asymptote $6s+6d$ or even higher. Unfortunately, the accuracy of the relevant difference-potential curves in this high-energy region

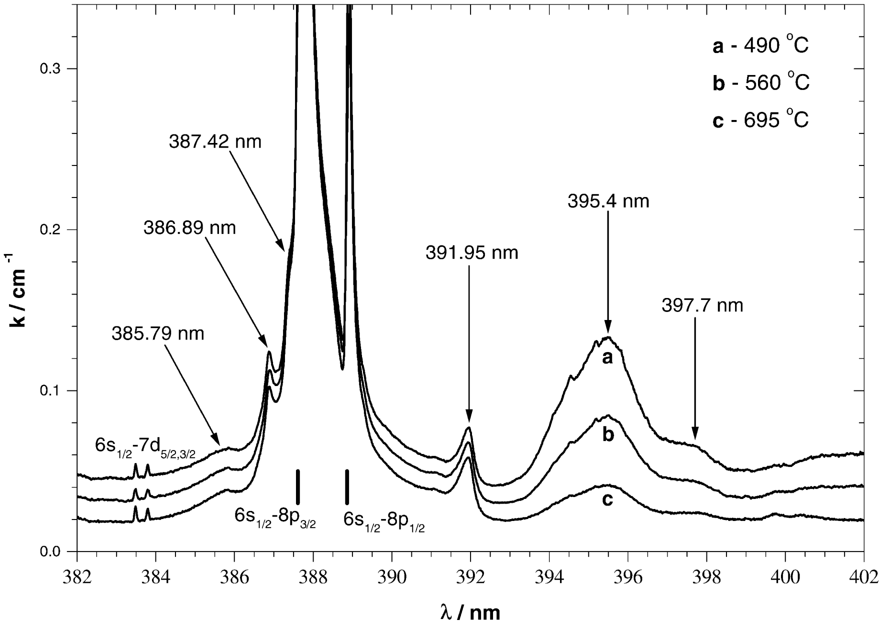

Fig. 3. The cesium-vapor absorption coefficient for the temperatures of the vapor at 490°C, 560 °C and 695 °C, in the wavelength range from 382 nm to 402 nm

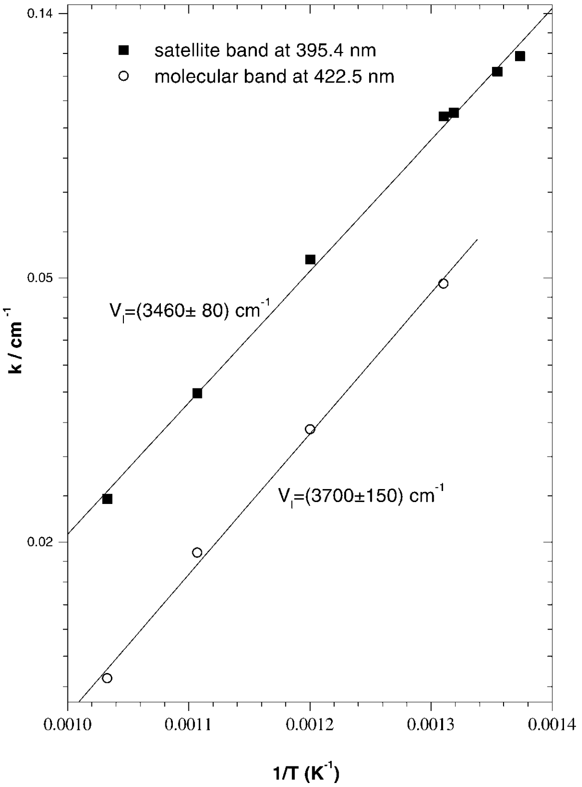

Fig. 4. The temperature dependence of the absorption coefficients in the ln scale, for the Cs_2 molecular band peaking at 395.4 nm and the second, much broader Cs_2 molecular band peaking at 420 nm, which reveal the dissociation energy of the ground state

is either not sufficiently good or there is a lack of calculated potential curves. This prevents easy identification of any observed satellite band with a particular extremum in the difference-potential curve. The Cs_2 absorption band peaking at 420 nm consists of several contributions consisting of Cs_2 $5\,^1\Sigma_u{}^+ \leftarrow 1(X)\ ^1\Sigma_g{}^+$, $4\,^1\Sigma_u{}^+ \leftarrow 1(X)\ ^1\Sigma_g{}^+$, $5^1\Pi_u \leftarrow 1(X)\ ^1\Sigma_g{}^+$ and $4^1\Pi_u \leftarrow 1(X)\ ^1\Sigma_g{}^+$ singlet transitions, as will be discussed below in connection with Fig. 5.

3 Discussion

It is difficult at present to assign all the features to the particular difference potential, especially because there are not precise calculations for all those potential curves which include the spin–orbit effect. However, it is quite clear that the near-wing satellite bands definitely stem from the photoassociation of cesium atoms at large distances into the long-range bound states of the Cs_2 molecule with a very broad potential well. The relevant difference-potential curves also possess a minimum (since the ground state is essentially flat at large distances), which produces a very pronounced maximum or a satellite band in the quasistatic wings. It would be interesting to extend theoretical calculations for even higher asymptotes than $7p+6s$ and $6d+6s$, with inclusion of the spin–orbit interaction.

In Fig. 5 we present the available difference-potential curves derived from ab initio calculations by Spies and Meyer [12] (left panel) and the Cs_2 absorption-coefficient curve in the UV–violet spectral region (right panel). Singlet states could be considered as reliable states for the prediction of the satellite bands around $8p-6s$ lines. From this figure nothing conclusive could be drawn. There are many maxima and minima and one interesting inflection, which could be responsible for the appearance of the singlet satellite band at 395.4 nm, provided the corresponding transition-dipole moments are sufficiently large.

It is obvious that more detailed and more accurate calculations are needed which involve even higher Cs_2 asymptotes and inclusion of the spin–orbit interaction. We hope that satellite bands observed and discussed in the present work could provide additional tests for these future studies.

Quite recently, NICHIA is offering UV LEDs peaking at about 370 nm and having a spectral width of only 12 nm. Different UV LEDs could have slightly shifted peaks, and

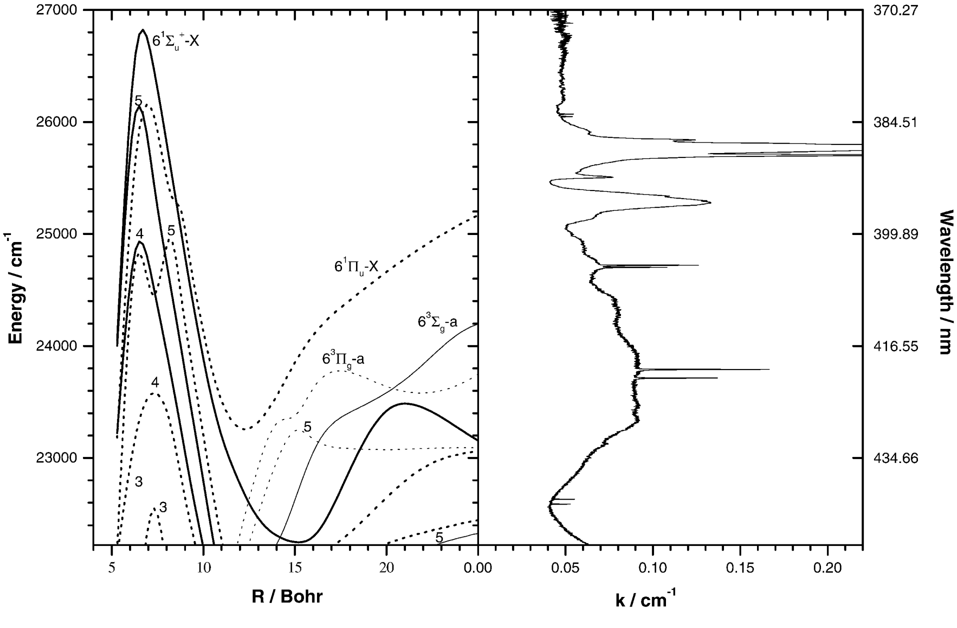

Fig. 5. a Cs_2 difference-potential curves from Spies and Meyer ab initio calculations. *Full lines*: $^1\Sigma_u{}^+ - 1(X)\ ^1\Sigma_g{}^+$ difference potential curves, *thick full lines*: $^3\Sigma_g{}^+ - 1\,(a)\ ^3\Sigma_u{}^+$ difference potential curves, *dot lines*: $^1\Pi_u - 1(X)\ ^1\Sigma_g{}^+$ difference potential curves and *thick dot lines*: $^3\Pi_g - 1(a)\ ^3\Sigma_u{}^+$ difference potential curves. **b** The Cs_2 absorption coefficient curve in the UV–violet spectral region

therefore the use of several such light sources can provide a broader continuum in this particular spectral region. Thus we may perform absorption measurements in the neighborhood of the Cs $6s-9p$ principal series line, where the ratio of the oscillator strengths in a doublet is already about 12 [13].

4 Conclusion

In this work we showed that due to the very effective thermal dissociation of Cs_2 molecules the temperature-independent diffuse spectral features can be distinguished from the bound Cs_2 molecules, which exhibit temperature dependence of the absorption coefficient. These temperature-independent spectral features or satellite bands stem from the photoassociation of triplet or singlet Cs–Cs pairs (free-to-bound transitions) or free-to-free transitions in the long-range region of interatomic distances.

We have shown that the new bright UV–violet LED with strong ultraviolet continuum at higher electric currents can serve as a very convenient continuous light source in the spectral region where the spectrum of a standard halogen lamp becomes very weak.

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