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Photoassociation of cesium atoms into $\mathrm{Cs_2}\ 3\,{}^3\Pi_\mathrm{g}$ state at $543.5\ \mathrm{nm}$

T. Ban, H. Skenderović, R. Beuc and G. Pichler
Institute of Physics - POB 304, HR-10000 Zagreb, Croatia

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Abstract. – We report absorption measurements in pure cesium vapor at high temperatures, when triplet absorption bands in the spectral interval 540–560 nm emerge within the singlet molecular bands which slowly diminish due to efficient thermal dissociation. The absorption bands have been identified as stemming from extrema in the $\mathrm{Cs_2}$ 3 ${}^3\Pi_\mathrm{g}$-a ${}^3\Sigma_\mathrm{u}^+$ difference potential curve. We performed a quasiclassical simulation which agrees well with experimental observation. Since the $\mathrm{Cs_2}$ a ${}^3\Sigma_\mathrm{u}^+$ state is only weakly bound, the observed absorption bands at 543.5 and 557 nm represent free-bound transitions or the photoassociation process.

Introduction. – Excited states of the $\mathrm{Cs_2}$ molecule are not well known either experimentally or theoretically, since the large spin-orbit splitting in the 6*p* level ($554.11\ \mathrm{cm^{-1}}$) affects coupling of the angular momenta and thus enlarges the number of states enormously. Dating from 1989 *ab initio* potential curves of W. Meyer and N. Spies [1, 2] have greatly facilitated the interpretation of cesium dimer spectra. However, when treating highly excited molecular states the difficulties increase substantially. In such a situation experimental conditions can be helpful in which the temperature is so high that only cesium atoms are present in the vapor and the photoassociation process dominates. We may expect that these free-bound transitions will be enhanced whenever the relevant difference potential curves have extrema. These extrema will be responsible for the formation of "diffuse bands" at smaller internuclear distances [3, 4] or "satellite bands" at larger internuclear distances [5]. The collisions in hot atomic cesium vapor will statistically prefer encounters within the lowest triplet state, and the molecular spectrum will be dominated by the diffuse bands belonging to the triplet manifold. The extreme case of such atomic hot vapor was presented in a paper by Erdman *et al.* [6] on the observation of the triplet satellite band at 603 nm that belongs to the $\mathrm{Li_2}$ 1 ${}^3\Pi_\mathrm{g} \leftarrow$ 1 (a) ${}^3\Sigma_\mathrm{u}^+$ difference potential having a pronounced maximum at an interatomic separation of 10 bohr. Previous observation of this satellite band was much more difficult due to the overlap with strong and dense $\mathrm{Li_2}$ 1 (A) ${}^1\Sigma_\mathrm{u}^+ \leftarrow$ 1 (X) ${}^1\Sigma_\mathrm{g}^+$ spectral lines [7].

It was recently shown that thermal dissociation of cesium dimers could be very effectively carried out in a cell by a c.w. laser tuned close to atomic resonance [8]. However, an easier and more effective way to suppress cesium dimers is to use a sapphire cell filled with cesium subjected to high oven temperature. With the use of such a sapphire cell Sarkisyan *et al.* [9] dissociated up to 85% of cesium dimers.

Tam *et al.* [10] measured the emission spectra of alkali-noble-gas systems with an argon-ion laser, and they reported two weak bands at approximately 542.5 nm and 557 nm which they identified as a $\mathrm{Cs_2}$ dimer emission. In the spectral region from 540 to 560 nm Huennekens *et al.* [4] observed an unknown double-peaked continuous spectral feature in the fluorescence excited by Cs 6*s*-7*p* laser excitation, and they presented convincing arguments of their $\mathrm{Cs_2}$ triplet nature. In a similar experiment but with argon visible laser lines Polly *et al.* [11] did

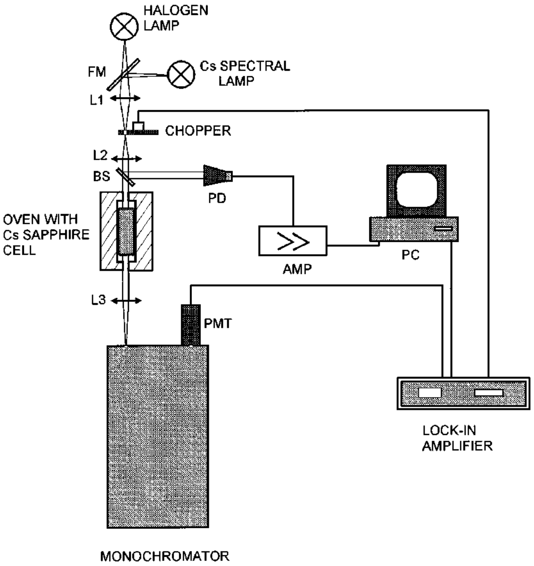

Fig. 1. – Experimental setup for absorption measurements. PMT is the photomultiplier, PD the photodiode, FM the folding mirror, BS the beam splitter, AMP the amplifier, PC the personal computer and L1, L2 and L3 are lenses. BS and AMP were used for monitoring the halogen lamp intensity.

not report any spectral feature in the 540–560 nm interval although in their figs. 2a, 2b and 2c we can discern a very weak emission band at approximately 543 nm. In another work of Polly *et al.* [12] a very weak band at approximately 543 nm is observable when the excitation laser wavelength was 476 nm (fig. 1 in ref. [12]).

We present here our measurements with a sapphire cell filled with a limited amount of cesium. We performed high-resolution absorption scans at different temperatures up to 750 °C. The significant thermal dissociation of $\mathrm{Cs_2}$ molecules at the highest temperatures was sufficient for two triplet diffuse bands to emerge from the otherwise dominant bound-bound $\mathrm{Cs_2}$ spectrum. The observed absorption peaks at 543.5 nm and about 557 nm are assigned to extrema in the $\mathrm{Cs_2}$ $3\,^3\Pi_\mathrm{g} \leftarrow 1(\mathrm{a})^3\Sigma_\mathrm{u}^+$ [1, 2] difference potential curve.

Experiment. – The experiments have been performed using a standard absorption setup, which is shown in fig. 1. The main part of the setup is an oven with a sealed-off cylindrical all-sapphire cell (ASC) containing cesium vapor. The advantages of the ASC over metallic and glass cells are: the possibility to operate at high temperatures (up to 800 °C), better homogeneity of temperature and density in the vapor column, well-defined vapor column length and simplicity of use. The length of the ASC used in these experiments was 160 mm, with an internal diameter of 10 mm and external diameter of 13 mm. Windows of the ASC were also sapphire, with transparency range between 160 nm to 7 μm. The residual vacuum in the ASC was about 10^{-3} Torr. Inside the cell was a tablet of a mixture of powders of $\mathrm{Cs_2Cr_2O_7}$ and Ti. This mixture provides 0.6 mg of pure cesium. The ASC is very sensitive to abrupt temperature gradients, so the temperature of the ASC must be changed slowly (during heating and especially when cooling down from high temperatures). The oven consists of a quartz tube wound with nichrome wire. The quartz tube is thermally isolated by a firebrick. The temperature was measured by a thermocouple positioned at the middle point of the ASC. The optical axis of the sapphire window was perpendicular to the surface [13].

During the initial heating a saturated cesium vapor appears in the ASC. The vapor consists

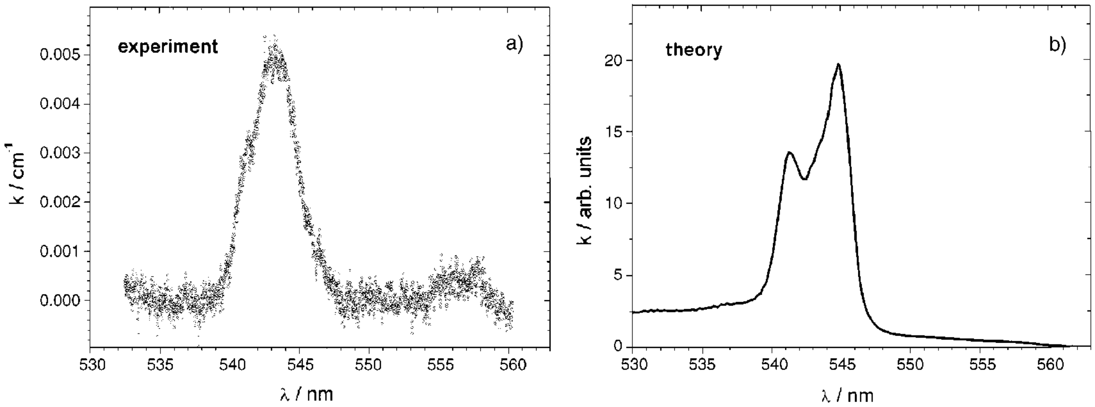

Fig. 2. – The comparison of the measured (a) and calculated (b) absorption coefficient of the Cs_2 543.5 nm band for $T = 727$ °C.

of cesium atoms and a few percent of Cs_2 molecules in thermal equilibrium with liquid cesium. We measured the largest Cs_2 molecular absorption at $T_0 = 422$ °C. At higher temperatures molecular absorption decreased which indicates that the whole amount of cesium is evaporated at T_0. In the regime of constant amount of cesium in the vapor phase, the temperature dependence of the chemical equilibrium constant $K(T)$ for the atom-dimer equilibrium favors dimer destruction with increasing temperature. Raising the temperature the atom number density slightly rises at the expense of dimer reduction.

The sapphire cell was irradiated by the continuous light from a halogen lamp. The light passing through the absorption cell was spectrally analyzed using a Jobin Yvon THR 1.5 m grating spectrometer equipped with Hamamatsu R936 photomultiplier. The output signal was fed into a Stanford Research SR510 lock-in amplifier and stored in a PC. The absorption spectrum was scanned by a rotating holographic grating (1200 grooves/mm) with computer-controlled stepper motor. The resolution of the system was 0.035 nm with 20 μm slit widths.

The absolute calibration of the wavelength scale was determined using a cesium low-pressure spectral lamp. Five independent sequential scans were taken for constant cell temperature. The average of these five scans gives the absorption profile with significantly reduced statistical noise.

Results. – We performed high-resolution absorption measurements using the ASC heated to different temperatures up to 755 °C in the wavelength region between 520 and 630 nm, where Cs_2 $2(D)^1\Sigma_u^+ \leftarrow 1(X)^1\Sigma_g^+$ bound-bound transitions occur. At the highest temperatures, because of the dimer dissociation, the absorption due to the Cs_2 $2(D)^1\Sigma_u^+ \leftarrow 1(X)^1\Sigma_g^+$ band was substantially reduced; and a new absorption band appears peaking at 543.5 nm together with a small one peaking approximately at 557 nm (visible at highest temperatures only). The absorption coefficient of the Cs_2 543.5 nm band is shown in fig. 2a in the spectral interval between 530 and 563 nm, for a temperature of 727 °C. We noted a weak increase of the Cs_2 543.5 nm band absorption coefficient with increasing temperature. In the present figure the absorption coefficient of the Cs_2 543.5 nm band has been obtained by careful subtraction of the Cs_2 $2(D)^1\Sigma_u^+ \leftarrow 1(X)^1\Sigma_g^+$ band absorption coefficient [14] which has a maximum at 580 nm. In this whole temperature interval above 422 °C up to 750 °C the cesium number density change is negligible. Overheating the cesium vapor resulted in thermal dissociation of Cs_2 dimers which enabled easy detection of predominantly collision-induced spectral features. The bands at 543.5 nm and 557 nm are not the only bands that emerged at very high cesium vapor temperatures, whereas the singlet bands connected with the Cs_2 $1(X)^1\Sigma_g^+$ ground state

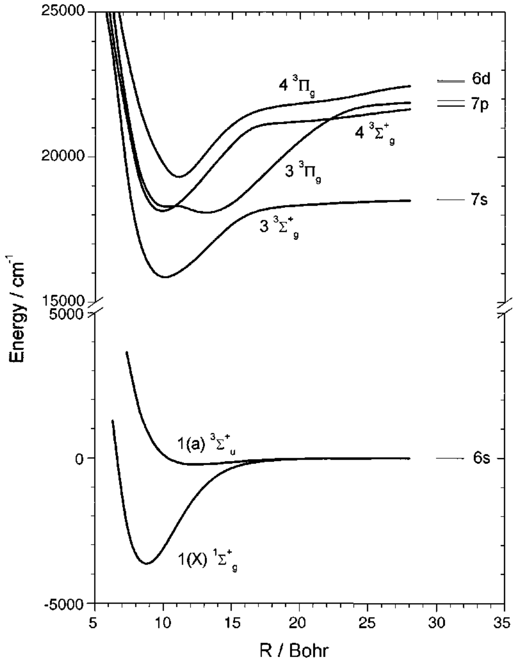

Fig. 3. – Relevant triplet potential energy curves of $\mathrm{Cs_2}$ states. The $\mathrm{Cs_2}$ $\mathrm{X}^1\Sigma^+_\mathrm{g}$ potential is shown for comparison.

gradually diminished in their absorption coefficient. In addition, there is an absorption band at 611.5 nm, which is a free-bound absorption $\mathrm{Cs_2}$ 3 $^1\Sigma^+_\mathrm{u} \leftarrow 1(\mathrm{X})^1\Sigma^+_\mathrm{g}$ spectral feature [15]. Numerous other satellite bands close to cesium atomic lines also emerge from the already weak discrete molecular spectrum, which will be reported in a separate publication.

In fig. 2b we present the theoretical simulation of the band at 543.5 nm, for the sake of comparison. This will be further discussed in the next section.

Discussion. – Potential curves from the triplet manifold of Spies and Meyer [1, 2] relevant for the interpretation of the $\mathrm{Cs_2}$ 543.5 nm band are shown in fig. 3. The difference potentials for some triplet and singlet potentials are shown in fig. 4 on the left-hand side. The $\mathrm{X} \rightarrow \mathrm{E}$ band in absorption is composed of several electronic transition contributions, but designation 3 (E) $^1\Sigma^+_\mathrm{u}$ was adopted from ref. [16]. On the right-hand side of fig. 4 the cesium transmission spectrum at 735 °C in the spectral region from 435 to 666.5 nm is presented. Judging from the positions of numerous extrema of the difference potential curves and matching with the position of the relevant diffuse bands (indicated by the arrow in fig. 4) it appears that the $\mathrm{Cs_2}$ 3 $^3\Pi_\mathrm{g}$ state is responsible for the formation of the 543.5 nm band. It is quite important to note that the $\mathrm{Cs_2}$ 3 $^3\Pi_\mathrm{g} \leftarrow 1(\mathrm{a})^3\Sigma^+_\mathrm{u}$ difference potential curve possesses four extrema, of which two (one minimum and one maximum) lie in the vicinity of 18300 cm^{-1} producing the 543.5 nm band, and the other two are close to 18000 cm^{-1} producing the weaker band at 557 nm. In addition to this the $\mathrm{Cs_2}$ 4 $^3\Sigma^+_\mathrm{g} \leftarrow 1(\mathrm{a})^3\Sigma^+_\mathrm{u}$ difference potential has two extrema at about 17600 cm^{-1} corresponding to a $\mathrm{Cs_2}$ 568 nm band. Huennekens *et al.* [4] observed this band as a very weak shoulder of strong 543.5 and 557 nm diffuse bands in their LIF spectra (see their fig. 10). In our highest-temperature absorption spectrum we could not clearly discern the $\mathrm{Cs_2}$ 568 nm band.

Spectral simulations as shown in fig. 2b indicate a very good agreement with experimental absorption spectra. The calculations have been carried out for a temperature of 727 °C. It can

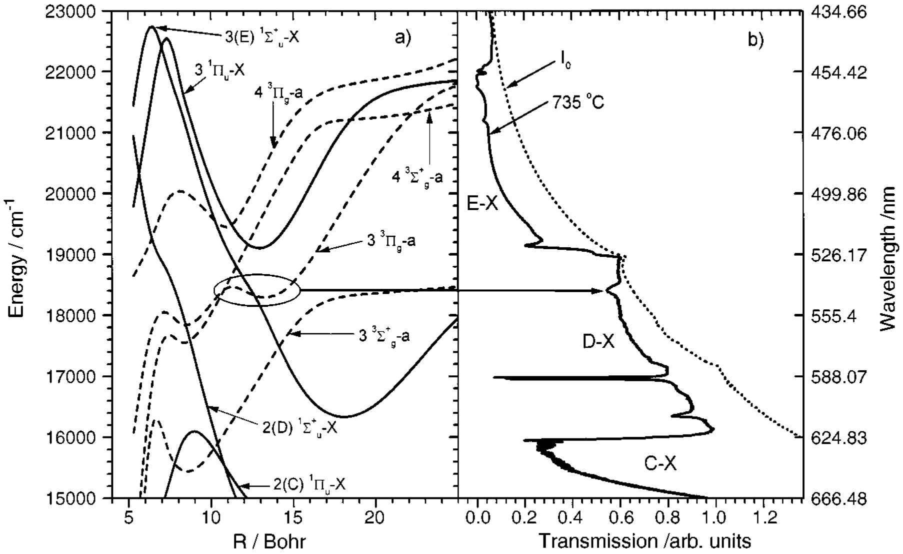

Fig. 4. – a) Triplet (dashed line) and singlet (solid line) difference potential energy curves of Cs_2 with transition energies in the 15000-23000 cm^{-1} range. b) Measured transmission spectrum at $T = 735$ °C in the same energy range as in fig. 4a. The dashed line denotes the transmission through the cold sapphire cell. The arrow indicates the correspondence beetwen outer extrema of the Cs_2 $3\,^3\Pi_g$ - 1 (a) $^3\Sigma_u^+$ difference potential and the observed band at 543.5 nm.

be readily observed that the Cs_2 $3\,^3\Pi_g \leftarrow 1(a)^3\Sigma_u^+$ difference potential curve reproduces the 543.5 and 557 nm bands. Since the Cs_2 $3\,^3\Pi_g$ potential curve actually consists of three separate potential curves (2_g, 1_g, and degenerate 0_g^+ and 0_g^- states), we assumed that the separation of the Cs_2 $3\,^3\Pi_g$ state into three potential curves is governed by the spin-orbit splitting from the Cs $6d$ asymptotic level. The reason why we estimated the spin-orbit interaction from the Cs $6d$ asymptotic level and not from the Cs $7p$ asymptotic level can be seen in fig. 3. An avoided crossing between the $3\,^3\Pi_g$ and $4\,^3\Pi_g$ potential curves takes place at an internuclear separation of about 25 bohr. If it were not for this local two-state interaction the $3\,^3\Pi_g$ potential curve would go smoothly to the $6d$ asymptote. For the absorption coefficient calculations we used the following formula [17]:

$$k(\omega,T) \propto \left\langle \left| \int_{-\infty}^{\infty} \mathrm{d}t D(t) \exp\left[(i/\hbar)\left[\int_{-\infty}^{t} \mathrm{d}t'\Delta V(t') - \omega t\right]\right]\right|^2 \right\rangle_{b,E}, \tag{1}$$

where $\Delta V(t)$ is the relevant difference potential curve and $D(t)$ is the transition dipole moment, which was, for the present calculation, taken as a constant in the entire internuclear separation region of interest. The time integration was performed using a classical trajectory defined by the impact parameter b and the asymptotic kinetic energy E. The final value of the absorption coefficient was summed over the impact parameter b up to $b_{\max}$ (which corresponds to the rotational quantum number $J = 600$) and averaged over the kinetic energy for the temperature $T = 727$ °C. In this procedure we calculated the contribution of the free initial states only. This is justified because the mean kinetic energy of the colliding cesium atoms is about three times larger than the depth of the Cs_2 $1(a)^3\Sigma_u^+$ initial state. A very similar procedure was carried out for the calculation of the emission coefficient (see fig. 5a). The emission from the Cs_2 $3\,^3\Pi_g$ state was calculated by taking into account the contribution of free initial states only. This was sufficient for comparison between theoretical emission shape and experimental

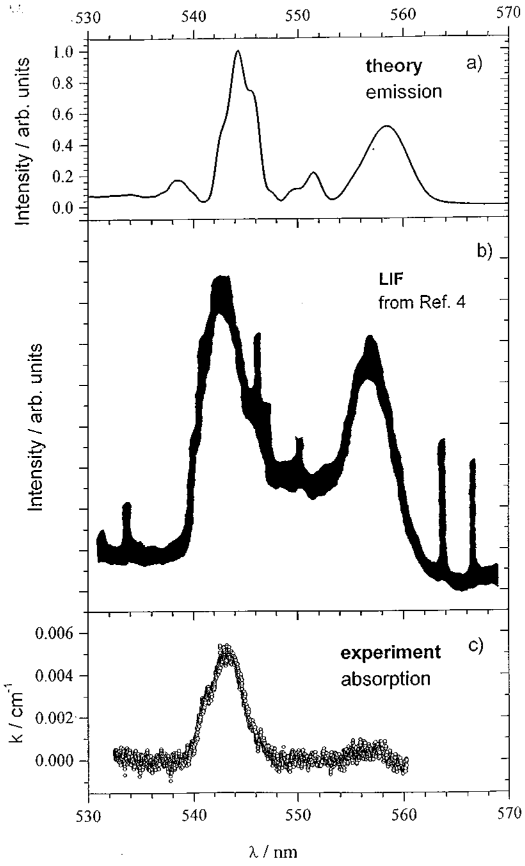

Fig. 5. – The comparison of the calculated emission profile (a), with the fluorescence spectrum observed by Huennekens *et al.* [4] (b), at temperature T = 360 °C for the wavelength range from 530 nm to 570 nm. In panel c the absorption coefficient from fig. 2a is replotted for comparison.

emission shape of Huennekens *et al.* [4] where the excitation was to the asymptotic atomic energy level. The present difference potential Cs_2 3 $^3\Pi_g \leftarrow 1(a)^3\Sigma_u^+$ is an interesting example of a multi-Condon point difference potential, which was also discussed by Veža *et al.* [5] for the satellite bands associated with Cs_2 1 $^3\Pi_g \leftarrow 1(a)^3\Sigma_u^+$ transitions.

In fig. 5a and b we compare the calculated emission profile with the laser-induced fluorescence (LIF) spectrum observed by Huennekens *et al.* [4] at T = 360 °C. This comparison is shown for the wavelength region from 530 nm to 570 nm. Figure 5b is an enlarged portion of fig. 10 from ref. [4]. The matching of diffuse band peaks at 543.5 nm and 557 nm is satisfactory considering all the approximations used in our calculations. However, calculated peaks (fig. 5a) are shifted towards longer wavelengths by about 60 cm^{-1}. In fig. 5c we replotted our absorption profile in order to show the coincidence of the measured peaks in absorption and emission. This is possible only when the structure of the bands is governed by the extrema in the relevant difference potential curves. Thus, the outer two extrema (one minimum and one maximum) in the Cs_2 3 $^3\Pi_g \leftarrow 1(a)^3\Sigma_u^+$ difference potential are responsible for the band peaking at 543.5 nm (see fig. 4), whereas the inner extrema at shorter internuclear separations contribute to the diffuse band peaking at 557 nm. The later is extremely weak in absorption since the Cs_2 $1(a)^3\Sigma_u^+$ potential is already repulsive at this location by about 2000 cm^{-1}, meaning that the number of absorbing pairs is very small. Therefore, we can observe it in our absorption experiment only at the highest temperatures, when the kinetic energy of some colliding pairs attains 2000 cm^{-1}. In the LIF observations of Huennekens *et al.* [4] there is no such constraint connected with the velocity of the colliding Cs atoms, since they are excited by c.w. laser light at 455 nm or 459 nm directly into the $7p\ ^2P_{3/2}$ and $7p\ ^2P_{1/2}$ asymptotes. The emission from the free $\mathrm{Cs}_2\ 3\ ^3\Pi_\mathrm{g}$ states gives an extended spectrum because the turning point of the free state is at smaller internuclear distances than locations where the extrema in the $3\ ^3\Pi_\mathrm{g} \leftarrow 1(\mathrm{a})^3\Sigma_\mathrm{u}^+$ difference potential responsible for the Cs_2 557 nm band occurs. Thus all four extrema in the $\mathrm{Cs}_2\ 3\ ^3\Pi_\mathrm{g} \leftarrow 1(\mathrm{a})^3\Sigma_\mathrm{u}^+$ difference potential curve are involved in the formation of the diffuse band emission spectrum with 543.5 nm and 557 nm peaks.

Conclusion. – We show that bound-bound and free-bound transitions form the Cs_2 543.5 nm and 557 nm absorption bands. At very high temperatures in our experiment the dominant contribution belongs to the free-bound transitions, since the dissociation energy of the $\mathrm{Cs}_2\ 1(\mathrm{a})^3\Sigma_\mathrm{u}^+$ (triplet ground state) is only about 230 cm^{-1}. Thus we have photoassociation processes that lead to the formation of the $\mathrm{Cs}_2\ 3\ ^3\Pi_\mathrm{g}$ state. Photoassociation is a very important process for production of ultracold potassium molecules in their ground states [18]. It would be of high interest to study whether these bands at 543.5 and 557 nm could be used for the detection of ultracold Cs_2 molecules. Three Cs_2 diffuse bands at 707, 713 and 718 nm have already been used by Fioretti *et al.* [19] for $\mathrm{Cs}_2\ 1(\mathrm{a})^3\Sigma_\mathrm{u}^+$ ultracold molecule detection.

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