Collision-induced photodissociation of the $3 \, {}^{1}\Pi_{\mu}$ state of Cs₂

J. J. Ho,* Chongye Wang, and R. A. Bernheim

Department of Chemistry, Penn State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

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Excitation of the $3 \Pi_{\mu} - X \Sigma_{g}^{+}$ transition in Cs₂ by the 476.5-nm line of an argon-ion laser in the

presence of inert gases results in emission from the $7p \, {}^2P_{3/2}$ and $7p \, {}^2P_{1/2}$ atomic states of Cs. This verifies $6s \, {}^2S_{1/2} + 7p \, {}^2P$ as the dissociation products of $3 \, {}^1\Pi_u$ and a dissociation energy of 4730.5 ± 0.8 cm⁻¹ for the $7p \, {}^2P_{3/2}$ limit or 4911.5 ± 0.8 cm⁻¹ for the $7p \, {}^2P_{1/2}$ limit.

A rich fluorescence spectrum is produced when cesium vapor is excited by the lines of an argon-ion laser.¹⁻¹⁰ Besides emission from several Cs₂ molecular states, atomic Cs emission is also observed. The addition of inert gases results in a decrease in molecular fluorescence and an increase in atomic emission as well as the production of Cs-inert-gas excimer emission.^{4,8} Two of the electronic states of Cs₂ that are excited by the argon-ion laser lines have been identified as $E^{1}\Sigma_{u}^{+}$ and $3^{1}\Pi_{u}$, and their molecular constants have been determined.¹¹⁻¹⁴ The $E^{1}\Sigma_{u}^{+}$ state at T_{c} =20195.32 cm⁻¹ correlates with the 6s ${}^{2}S_{1/2}$ + 7s ${}^{2}S_{1/2}$ Cs atomic states giving a dissociation energy of 1987.7±0.8 cm⁻¹. The 476.5-nm line of the argon-ion laser apparently excites only the $3^{1}\Pi_{u}$ state at 20 685.669 cm⁻¹. The purpose of the present study is to obtain the identity of the atomic dissociation products of the $3^{1}\Pi_{u}$ state and thereby the dissociation energy.

It has been found that the $3 {}^{1}\Pi_{u}$ state is predissociated by an unbound ${}^{3}\Sigma_{u}$ state to produce $5p {}^{2}D_{3/2,5/2}$.^{6,7} It is also known that collisional-induced dissociation is common in the alkali-metal dimers.¹⁵ Here it is established that the collisional-induced dissociation of the $3 {}^{1}\Pi_{u}$ state results in the production of both $7p {}^{2}P_{3/2}$ and $7p {}^{2}P_{1/2}$ fine-structure states of Cs.

The experiments were performed on 99.95%-pure Cs contained in a 100-cm³ Pyrex bulb over the temperature range 453–588 K, corresponding to Cs atom densities of $10^{14}-10^{16}$ cm⁻³. Added inert-gas densities ranged from 0 to 10^{19} cm⁻³. Excitation was produced with an unfocused argon-ion laser operating on a single line but with multimode output at 476.5 nm and power levels between 0.8 and 2 W. Fluorescence collected at 90° to the laser-beam propagation direction was dispersed with a Jarrell-Ash 25-100 series Czerny-Turner double monochromator operating with a resolution of 5 cm⁻¹. A lock-in amplifier was used in the detection.

The fluorescence spectrum displays the many Cs_2 molecular bands that have been studied in other laser excitation studies. Of the features that depend upon the presence of inert buffer gases, the Cs-*M* excimer band at 17 500-18 000 cm⁻¹ (for M = Ar) has been reported using 457.9-nm excitation.⁴ Besides the previously observed effects that result from the influence of added buffer gases, the production of the $7p \, {}^2P_{3/2,1/2} \rightarrow 6s \, {}^2S_{1/2}$ doublet (21 946.66 cm⁻¹ and 21 765.65 cm⁻¹) (Ref. 16) was

found when the Cs vapor was excited by the unfocused 476.5-nm (20987-cm^{-1}) argon-ion laser line. The doublet does not occur in pure cesium vapor excited under identical conditions. A study of its dependence on the power \mathcal{P} of the 476.5-nm exciting radiation, $I = [\mathcal{P}]^n$, gives a value of $n = 1.03 \pm 0.02$ for all inert gases used (He,Ne,Ar,Kr) indicating a one-photon process. When the 476.5-nm radiation is focused into the sample cell to give a highpower density, these as well as other atomic transitions are observed regardless of the presence of an inert buffer base. In this situation they are due to various nonlinear processes such as multiphoton ionization of Cs₂ to form $Cs_2^+ + e$, followed by dissociative recombination to form excited atomic states of Cs. For example, the $7d^2D_{5/2} \rightarrow 6s^2S_{1/2}$ transition appears under focused, high-power excitation and has a \mathcal{P}^n dependence with $n = 1.93 \pm 0.02$. While these latter effects have been observed and discussed previously,¹⁷ the production of the $7p^2P_{3/2}$ and $7p^2P_{1/2}$ states by a one-photon process in the presence of buffer gases is a new observation and proceeds by an inert-gas collision-induced process.

Examples of the appearance of the $7p \, {}^{2}P \rightarrow 6s \, {}^{2}S_{1/2}$ transitions are shown in Fig. 1. Both the Cs-Ar and Cs-Kr systems display significant spectral wings to the red, which can be attributed to the strong van der Waals wells that exist for the ground and excited states for these species.^{18,19} Significant spectral wings are not apparent for Cs-He and Cs-Ne, although the Cs-He system does



FIG. 1. Cs $(7p^{2}P)$ doublet emission produced by inert-gas collision-induced dissociation of the $3^{1}\Pi_{u}$ state of Cs₂. Arrows mark the positions of the fine-structure components.

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TABLE I. Pressure dependence of the integrated intensity of the Cs $(7p^2P_{1/2,3/2} \rightarrow 6s^2S_{1/2})$ atomic transitions for different noble gases at 553 K with *n* defined in the text. Uncertainties are standard deviations.

Gas	He	Ne	Ar	Kr
<u>n</u>	1.2±0.1	0.83±0.05	1.69±0.06	1.31±0.05

exhibit broadening in the temperature range studied. The positions of the unperturbed $7^2P_{3/2}$ and $7^2P_{1/2}$ atomic lines are clearly seen as self-reversed features and are due to the Cs-atom density surrounding the excitation region.

A measurement of the intensity of the $7p^2P$ atomic spectral lines as a function of buffer-gas pressure was made. Table I shows a fit of the intensities to an expression $I = KP^n$ where I is the integrated intensity, K is a constant, and P is the inert gas pressure. Measurements were made between 40 and 400 Torr for He, Ne, and Ar and between 40 and 250 Torr for Kr. The values of n for He and Ne are near unity, implying a single collision for the rate-determining step for production of excited $7^2 P$ atoms. The larger values for Ar and Kr indicate that the process is more complex, requiring more collisions to produce dissociation of the excited state. This may be due to the emerging importance of the strong potential wells for the ground and excited states of Cs-Ar and Cs-Kr. A concomitant decrease in intensity of the Cs₂ molecular fluorescence (observed on the blue side of the 476.5-nm exciting radiation) was found in all cases for increased buffer-gas density. C_{2} 7² P

Cs $7^{2}P$ production is also found with the 488.0 and 457.9-nm argon-ion laser lines, but only weakly with 514.5-nm lines. This is consistent with the fact that radiation at 514.5 nm can only excite the $B^{1}\Sigma_{u}^{+}$ state of Cs₂ and not the $3^{1}\Pi_{u}$ state.^{13,14} There is also no variation in the relative intensities of the $7p^{2}P$ doublet with either temperature or pressure. In this respect the collisional-induced dissociation differs from that observed in the $B^{1}\Pi_{u}$ state of Li₂, where fine-structure selectivity is observed and found to vary with pressure.¹⁵

It has been suggested⁵ that $6s^2S_{1/2} + 7p^2P_{1/2}$ are the dissociation limits of $3\,^1\Pi_u$. The present results show that $6s\,^2S_{1/2} + 7p\,^2P_{3/2}$ is also a possibility. Therefore the dissociation energy of $3\,^1\Pi_u$ is 4730.5 ± 0.8 cm⁻¹ for the $7p\,^2P_{1/2}$ limit and 4911.5 ± 0.8 cm⁻¹ for the $7p\,^2P_{3/2}$ limit if the value of $D_e = 3649.5\pm0.8$ cm⁻¹ is taken for the ground-state dissociation energy.²⁰

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- *Present address: Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan, Republic of China.
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