



Photolytic spectroscopy of simple molecules. III. The selective photolysis of CsKr and Cs2Kr at visible wavelengths

C. B. Collins, F. W. Lee, H. Golnabi, F. Davanloo, P. A. Vicharelli, D. Popescu, and Iovitzu Popescu

Citation: The Journal of Chemical Physics **75**, 4852 (1981); doi: 10.1063/1.441922 View online: http://dx.doi.org/10.1063/1.441922 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/75/10?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Photolytic spectroscopy of simple molecules. V. Prompt and delayed photolysis of Cs2 excited at yellow wavelengths J. Chem. Phys. **82**, 4965 (1985); 10.1063/1.448670

Photolytic spectroscopy of simple molecules. IV. Prompt and delayed photolysis of equilibrium mixtures of Cs2, Cs2Kr, and CsKr producing Cs(52 D) at visible wavelengths J. Chem. Phys. **77**, 5455 (1982); 10.1063/1.443805

Photolytic spectroscopy of simple molecules. I. The production of 52 D atoms from Cs2 J. Chem. Phys. **74**, 1053 (1981); 10.1063/1.441238

Photolytic spectroscopy of simple molecules. II. The production of 6P atoms from the X 1Σ g state of Cs2 J. Chem. Phys. **74**, 1067 (1981); 10.1063/1.441212

Scattering of Low Velocity Neutral Particles: The Cs–He, Cs–Kr, and Cs–Xe Interactions J. Chem. Phys. **53**, 1270 (1970); 10.1063/1.1674127



Photolytic spectroscopy of simple molecules. III. The selective photolysis of CsKr and Cs_2Kr at visible wavelengths

C. B. Collins, F. W. Lee, H. Golnabi, F. Davanloo, and P. A. Vicharelli

Center for Quantum Electronics, The University of Texas at Dallas, Richardson, Texas 75080

D. Popescu and lovitzu Popescu

Central Institute of Physics, Bucharest/Magurele, Romania (Received 30 June 1981; accepted 28 July 1981)

In this work a two-photon technique was used for the measurement of the relative cross sections for the selective photolysis of an equilibrium distribution of CsKr and Cs₂Kr populations existing at 523 °K in the presence of 0.132 amagat Kr. The cross sections for photolysis that selectively produced the lowest four excited states of Cs were obtained. Over the wavelength range 420 to 660 nm, the resulting dispersion curves showed one major feature which could be attributed to CsKr, the $6s\sigma \rightarrow 5d\sigma$ band dissociating to produce $Cs(5 \,^{2}D_{s(2)})$. Various considerations indicated that the other structures observed in the spectrum belonged to the trimer Cs₂Kr formed from Cs₂ through the attraction of a Kr by polarization forces. The occurrence in the spectra of both CsKr and Cs₂Kr of relatively broad photolysis bands leading to extremely selective distributions of product state populations was found to be fairly common. As in the previous work with Cs₂ it was observed that adiabatic and hence, state-selective dissociation occurred if the photolysis was excited at a transition energy not too much in excess of the threshold for the process. An examination of the kinetics of the photolysis products gave rate coefficients for the mixing and quenching of the fine structure components of Cs (5 ²D) of 7×10^{-12} and 3.7×10^{-13} cm³ sec⁻¹, respectively. At the densities used in this experiment these implied that useful populations of single states of Cs could be photolytically pumped with broadband radiation for periods of the order of tens of nanoseconds, while populations of energy levels could be pumped for more than an order of magnitude longer period of time.

INTRODUCTION

A new multiphoton technique for the correlation of photolysis bands observed in the spectra of simple molecules with their dissociation products has been recently reported.¹ It was applied in a study of the state-selective photolysis of Cs₂ with extremely interesting results.^{2,3} In that work the implementation of this technique provided a powerful insight into the identity and location of several new dissociative states of importance to the photolysis of Cs_2 . Beyond the satisfaction of practical motivations associated with the identification of new media for photolytically pumped lasers, that and the related preliminary work⁴ provided the basis for several general conclusions about the prospects for the use of electronic transitions in laser chemistry. First, at least for Cs₂ the existence of broad spectral bands for photolysis that produced remarkably selective distributions of product state populations was found to be a fairly common occurrence. Second, the actual dissociation process seemed to occur adiabatically, and hence selectively, if the transition energy absorbed by the parent molecule was not too much in excess of the actual threshold for the process. Finally, the converse appeared to hold as well, in that for transitions which excited a considerable excess of energy in the unstable state of the parent, dissociation occurred nonadiabatically, and hence nonselectively, in agreement with previous observations of enhanced fluorescence excited by the photolysis of mercury halides. 5,6

In principle the method introduced in this recent work is straightforward. Two independently tunable dye lasers are synchronously pulsed and used to illuminate a vapor of the molecules to be studied. The first pulse dissociates the molecules of the sample along the various possible channels. Then a delayed pulse identifies the products by exciting them individually into easily detected Rydberg states in a time too short to permit collisional mixing or radiative cascading of the particular populations produced by the first pulse. The distinctive feature of this technique is this rapid detection of the direct products of photolysis, whose relative populations are unperturbed by subsequent relaxation chemistry. In contrast, the previous studies of Cs_2 had typically used cw dye lasers and so had included the collisional mixing of product populations to an undetermined degree.

While the photolysis spectrum of Cs_2 proved to be an intrinsically interesting demonstration of this new technique and what it could accomplish, the quantitative analyses of the resulting spectra were impeded by the paucity of theoretical estimates for the potential curves of Cs_2 . In contrast, the alkali-metal-inert-gas excimers offer a completely different perspective. Being essentially one-electron systems, they are computationally tractable and at the same time experimentally accessible.

Historically, the transitions between electronic states of such molecules were studied first as pressurebroadened⁷ lines of the constituent alkali atoms and subsequently as excimeric transitions.⁸ These early investigations were generally limited to molecular transitions correlated at large internuclear separations with allowed transitions in the alkali atoms. More recently, bands isolated from all atomic lines of the constituents have been discovered^{9,10} and attributed to transitions between molecular states that at large internuclear separation correlate with forbidden atomic transitions. Con-

128 114 34 22 On: Fri 28 Nov 2014 20:36:47

siderable effort has been expended in the investigation of such bands in absorption, $^{11-13}$ fluorescence, 14 and emission, 15,16 particularly for the excimers formed from the heavier alkali metals and the more polarizable inert gases.

A comprehensive tabulation of corresponding potential curves has been available^{17,18} for several years that has predicted a rich structure in the electronic transition spectra of the alkali-metal-inert-gas molecules. However, only more recently have attempts been made to quantitatively confirm the theory and these have immediately led to controversies.¹² For example, in the energies of molecular terms originating from Xe +Cs(5D_{5/2}) and Xe +Cs(7S_{1/2}), disagreements as great as 2000 cm⁻¹ at values of internuclear separation important in absorption at reasonable thermal energies have been found. In fact, agreement has been obtained only on the most coarse aspects of the spectrum.

These rather negative results apparently provided the motivation for an exemplary study undertaken with the best of the conventional techniques of the spectral bands attributed the transitions¹⁹ $6s\sigma - 7s\sigma$ and²⁰ $6s\sigma - 5d\sigma$ in CsX molecules, where X was an atom of an inert gas. In this most recent work the molecular transition was again excited by a cw dye laser and then detected by collecting the fluorescence from dissociation products of the excited molecular state. However, the time delay between the steps of excitation and detection was uncontrolled and may have been long on the time scale of the relevant excited state chemistry. Potential curves were unfolded from the band spectra and were found to agree with neither the theoretical results of Pascale and Vandeplanque^{17,18} nor the most recent calculations of Czuchaj and Sienkiewicz.²¹

The possibility for an anomalous distortion of the absorption bands of an excimer such as CsKr by overlapping contributions from the trimer CsKr₂ was examined²² and shown to be ngeligible at the inert gas pressures generally used in the experiments of Sayer *et al.*^{19,20} However, the suggestion¹³ that significant levels of absorption from the trimer Cs₂Kr might tend to obscure many of the spectral features of CsKr seems to have passed unnoticed.

The work reported here concerns an examination of the selective photolysis of cesium-krypton molecules. The same techniques that had proven successful with Cs, were employed with remarkable results. Most of the dominant spectral features generally attributed¹² to CsKr were concluded to be the result of transitions in Cs₂Kr. In the red region of the spectrum the band previously identified²⁰ with the $6s\sigma - 5d\sigma$ transition of CsKr was determined to be a composite of that band which led through photolysis to the prompt production of $Cs(5^2D_{5/2})$ atoms and of a strong, unrelated band of Cs₂Kr leading through photolysis to the direct production of Cs(6² $P_{3/2}$). Except for the minor transition $6s\sigma - 6d\sigma$. previously identified¹³ with CsKr, no other photolysis band of CsKr could be found through the examination of the prompt products. The preponderance of structure in the spectrum that was contributed at nearly all visible wavelengths in this experiment by the trimer Cs2Kr could



rK. 1. Schematic representation of the multipliciton process used in this work for studying the selective photolysis of CsKr. Typical molecular potentials are plotted as functions of internuclear separation with radiative transitions shown by arrows. The first transition causing photolysis is designated (1a) for predissociation or (1b) for direct dissociation. The second transition used to excite the products, Cs*, to the readily ionized state Cs** is denoted (2), while (2') shows a possible transition for fluorescent detection.

explain the persistent disagreement between theory and experiment generally recorded in the literature.

METHOD

The work reported here made use of essentially the same experimental apparatus and analytical techniques described in the comprehensive report^{2,3} of the recent studies of the photolysis of Cs_2 . The relationship of this method to other methods used previously is best illustrated by Fig. 1. As shown there schematically, photolysis could occur through the excitation of a transition, such as (1a), to a bound state which could subsequently predissociate to produce Cs*. The principal restriction is that there must be an intersection at a suitable energy of the potential curve for that bound state with a curve for a repulsive state of the proper symmetry. The excitation of a transition, such as (1b), directly to a repulsive state correlated with the same dissociation limit would comprise an alternative channel for the production of Cs* by the photolysis of CsKr. In the Born-Oppenheimer approximation, the relative importance of channels (1a) and (1b), together with their dependences upon the wavelength of the source inducing the transition would depend upon the matrix element for the transition between the electronic states, the Franck-Condon factors de pending upon the initial and final states of the nuclear motion, the Hönl-London factors describing the probability for any changes in rotational motion, and upon the probabilities for spontaneous dissociation of the excited state formed. In principle, except for the last, these are well-known quantities whose product is the transi-

 Cs^++Kr



FIG. 2. Schematic representation of the experimental apparatus. The portion common to that used in the precursive study of C_{s_2} is enclosed by the dotted lines.

tion probability for that particular absorption band of CsKr. When multiplied by the last quantity and with an adjustment of numerical constants, it becomes the cross section for the photolysis of CsKr into the products Cs* + Kr. It is the measurement of this cross section that lies at the focus of the type of work reported here.

In the more elaborate studies undertaken previously^{19,20} with conventional techniques, the isolation of particular channels for photolysis was accomplished by experimentally correlating absorption data from transitions such as (1a) and (1b) in Fig. 1 with fluorescence radiation from a transition, such as (2') emitted from populations of atoms produced from the direct products of dissociation by cascade or by collisional processes. To be successful such a technique required; (1) that the probability for the emission of the fluorescence be high in comparison to the probability that the state would be quenched nonradiatively. (2) that the emission occur before collisional processes would transfer the excitation from some other product state into either Cs* or into the upper state radiating (2'), or the reverse, and (3) that the necessary relaxation of Cs^* into the upper state radiating (2') not be precluded by steps taken to satisfy the first two requirements. Generally, the degree to which the experimental situations conformed to these idealizations could not be unequivocally demonstrated.

The multiphoton technique used in this work overcame these difficulties and demonstrated a very high sensitivity for detection. The products of dissociation were detected through the absorption of a second photon in a transition such as (2) in Fig. 1. However, instead of attempting to detect the slight attenuation of an illuminating beam of wavelength corresponding to transition (2), the strategy of using the second transition to populate a relatively long-lived Rydberg state, Cs**, was employed. Then, as had been demonstrated in much earlier work, ²³ if that Cs** state were sufficiently close in energy to the ionization limit, it would have essentially unit probability for undergoing collisional ionization, either to Cs₂⁺ or to Cs⁺ + Cs⁻, through associative ionization as a component step, or to Cs⁺ by simple inelastic collisions with the majority species in the medium, even in the presence of 1 amagat inert gas.¹³ The resulting ionization was then detected in comparison to a back-ground ionization which tended to be intrinsically low.

The apparatus used in this work is shown schematically in Fig. 2. The primary photolysis system enclosed in dotted lines is the same as used in previous work^{2,3} with Cs₂. Basically, it consisted of two independently tunable dye lasers pumped by a single pulsed nitrogen laser. The output beams from the dye lasers were aligned to be spatially collinear, but were temporally dispersed so that the one used to dissociate the population of parent molecules arrived first at the absorption cell by an amount equal to the duration of the pulse. Provisions were available for the adjustment of the temporal separation of the pulses, but for the examination of the spectrum the interpulse delay was generally set to the minimum practicable value of 3 nsec in order to reduce the possibility for collisionally mixing the product populations. As expected, with a reversed temporal sequence the effect was completely absent. The linewidth of the output from the dye lasers was of the order of 0.01 nm and corresponded approximately to the resolution with which the wavelength could be set.

The additional dye laser system shown outside the

dotted enclosure in Fig. 2 was pumped by a separate N_2 laser, electrically synchronized through a variable delay with the N_2 laser pumping the primary photolysis system. The beam from this additional source was combined collinearly with the beams for photolysis and detection. However, since the electrical delay was arranged for the trigger pulse initiating the sequence of photolysis and detection, the pulse of supplementary illumination preceded the normal sequence by a time which could be set to a value between 20 and 1000 nsec. It was generally used to extend the range of times over which the delay between photolysis and detection of the products could be adjusted. With this modification the stability of the distribution of product state populations could be examined.

The occurrence of the overall sequence of photolysis was determined in this two-photon process by detecting the cesium ions produced in the vapor by the associative ionization of the populations of states produced from the dissociation products by the delayed laser pulse. The detection was accomplished by including a space-charge limited diode in the absorption cell. This method has been shown to be very effective for the products of the photoionization of metal vapors, even in the presence of densities of inert gases exceeding 1 amagat.¹³ Essentially, the technique uses the ionization in the vapor as a distributed grid to control a space-charge limited current flowing between a cathode and an anode arranged to contain the absorbing vapor between them. Sensitivites to the production of one ion per second have been achieved in this manner.²³ In the experiment reported here, the detecting diode was operated with the cesium vapor at a partial pressure of 0.13 Torr and the krypton at a density of 0.132 amagat.

By adjusting the wavelength of the delayed pulse to agree with a known absorption line corresponding to a transition to a Rydberg state of Cs* from a particular one of the possible dissociation products of the parent molecule as shown by transition (2) in Fig. 1, the cross section for photolysis into a channel leading to that specific product was isolated for measurement. The relatively narrow bandwidth of the absorption channel insured that the number of ions resulting from the subsequent associative ionization of the Rydberg atoms exceeded by 1.5 to 2 orders of magnitude the amount of ionization produced by any competing process such as the direct photoionization of the excited states of the various possible molecules remaining from the excitation produced by the first laser pulse. It was found that the composite effect of all of the spurious channels leading to the production of ionization that tended to contribute background signal and noise to the multiphoton process represented less than 20% of the total signal and, thus, could be readily subtracted without degrading the signal to noise ratio. Once corrected in this way, and provided that some care was taken to avoid intensities so excessive that one of the steps in the absorption sequence became saturated, an ion signal was obtained that was found to be linearly proportional to the intensities from each of the two lasers in the primary photolysis system. Essentially, then, this resulting signal was assumed to be proportional to the product of the intensities multiplied



FIG. 3. Dispersion curves as functions of wavelength of the delayed laser pulse for the ionization of the particular product states $Cs^*(5^2D_{3/2})$ and $Cs^*(5^2D_{5/2})$. The ionization resonances corresponding to transitions of the type $5^2D \rightarrow n^2F$ are specifically identified in the graph. Solid curves show the results of this experiment in comparison to the dotted curve obtained for pure Cs in Refs. 2 and 3. (a) Pressure broaden-ing and shifting caused by the addition of Kr which rendered inutile the transitions previously used in studies of the photolysis of Cs_2 . (b) Pressure broadened transitions found to be usable in this experiment.

by the known transition probability for the excitation of the dissociation product, the probability for the associative ionization of the resulting Rydberg population, and the cross section to be determined for the photolysis of the cesium molecule into that particular product channel. A more detailed analysis^{2,3} has been reported which quantitatively justified this procedure that was used in this work with the following refinement.

Attempts to simply extrapolate the previous measurements on Cs_2 were initially frustrated by the extreme broadening of the atomic transitions such as (2) in Fig. 1 that has been used for product detection in low pressure cesium vapor. Figure 3(a) shows the comparison between such transitions in pure cesium and in the presence of the 0.132 amagat density of krypton used in these experiments. As can be seen, for these particular transitions the fine structure could not be resolved. More isolated transitions were required and an example of those found to be satisfactory is shown in Fig. 3(b) on a different scale of wavelengths.

Unlike the case for the photolysis of Cs_2 , the linewidth of the detecting transition was larger than that of the laser and the algorithm used for analysis had to be modified slightly from the form derived as Eqs. (1) and (2) of Ref. 3, to obtain

$$\frac{b_1(\Delta\lambda)}{(E_1/\hbar\omega_1)(E_2/\hbar\omega_2)} \left\{ P_{C_s} * * \sigma_{C_s} * * (\lambda_2) \right\}^{-1}$$
$$= G[Cs_n X] \sigma_{C_s} * (\lambda_1) f_1(0) \int f_2(q) dq.$$
(1)

In this expression the measured ionization signal has been assumed to have maximum amplitude b_1 and fullwidth-half-maximum (FWHM) of $\Delta\lambda$, E_1 and E_2 are the energies in the pulses from laser 1 used to dissociate the molecules of $Cs_n X$ at wavelength λ_1 and from laser 2 used to excite the products from state Cs^* to Cs^{**} , respectively. The spatial distributions of the two beams are represented by f_1 and f_2 , respectively, and $\sigma_A(\lambda_n)$ denotes the cross section for the absorption at wavelength λ_n to produce the state A. The term G collects geometric factors while P_A denotes the probability of ionization of state A. The derivation of this expression is detailed in Refs. 2 and 3 except that because of the pressure broadening, b_1 has been replaced by $b_1(\Delta\lambda)$ in Eq. (1).

The quantity on the left hand side of Eq. (1) was evaluated from measurements of the ion signals b_1 and their widths $\Delta\lambda$, corrected for backgrounds and minor competing channels, as described in Refs. 2 and 3. It was obtained in this work for the photolytic production of $6^2P_{3/2}$, $5^2D_{3/2}$, and $5^2D_{5/2}$ by exciting the transitions $6^2P_{3/2}$ $+15^2D$, $5^2D_{3/2} + 31^2F$, and $5^2D_{5/2} + 23^2F$, respectively. Then, to within the extent that the remaining terms on the right hand side of Eq. (1) could be maintained as experimental invariants, the relative cross sections for photolysis, $\sigma_{Cs}^*(\lambda_1)$, could be obtained from a simplification of Eq. (1) yeilding

$$\sigma_{Cs}*(\lambda_1) = \frac{b_1(\Delta\lambda)}{E_1E_2} B_{re1}^{-1} \frac{480}{\lambda_1} , \qquad (2)$$

where cross sections were scaled to their relative values at 480 nm for convenience and B_{rol} denotes the collection of parameters appearing in Eq. (1) that could be obtained from the literature. Values for B_{rol} used in the reduction of this data were 1, 0.53, and 0.26 for the detection of Cs atoms in the $6^{2}P_{3/2}$, $5^{2}D_{3/2}$, and $5^{2}D_{5/2}$ states, respectively, through the excitation of the transitions listed above.

To minimize the effects of any drift of the alignment of the normalized overlap functions f_1 and f_2 , the beams were adjusted to different radii so that one could be completely contained within a region near the center of the other, where the variation of the latter was minimal, in order to agree with the product of spatial integrals shown in Eq. (1) rather than the integral of products which could be more sensitive to alignment.

RESULTS

Photolysis spectra

As in the previous study^{2,3} of Cs_2 , in order to establish the relative scale for the photolysis cross sections into the 6²P and 5²D product states, the measurements were alternated among all the product states at a single photolysis wavelength, 480 nm, in a sequence designed to eliminate systematic errors between the changes of dyes necessary for the excitation of the different product states. Once the relative magnitudes were determined at that reference wavelength, the cross sections for each of the product states were measured individually as functions of wavelength. As in the previous study, the measurements were made on a constant mesh of 2.5 nm with the linearity of the signal to changes of intensity and the overlap of the beams being periodically verified. The combined effects of nonreproduceability and scatter were found to be less than 30% and the values finally plotted at each transition energy were the averages of three to five separate determinations.

The resulting cross sections for the photolysis of cesium krypton molecules into three of the lowest four energetically possible products are shown in Fig. 4. The scales for the cross sections for the production of 6P and 5D states from CsKr are the same to facilitate direct comparison between them. No production of $6^{2}P_{1/2}$ was observed at any visible wavelength so the cross section for that channel of photolysis can be concluded to be less than 0.01 in the units of Fig. 4.

As in the case of Cs_2 , the photolysis channels appear to be concentrated into three spectral regions correlating with the red, yellow, and blue absorption bands of CsKr that had been reported¹² as a result of classical studies conducted at orders of magnitude of higher inert gas density. In fact, except for the red band for the production of $5^{2}D$ atoms at energies near 15800 cm⁻¹, the similarity between the photolysis bands for CsKr and Cs_2 is remarkable to an extent, raising questions about the identity of the actual parent molecules. For example, the yellow band attributed to CsKr at 17800 cm⁻¹ has been previously assumed¹⁹ to correlate, and hence dissociate, to $Cs(7^2S_{1/2}) + Kr$. However, the data of Fig. 4 shows this region to contain a composite of bands leading to dissociation or predissociation into $6^2 P_{3/2}$ and $5^2 D_{3/2}$ and $5^2 D_{5/2}$ in roughly the same relationships as observed in the photolysis of Cs_2 . This similarity can be appreciated more clearly from Fig. 5 where some of the data has been shown on a scale of wavelengths, together with the corresponding data for Cs₂.

The molecular state resulting from $Cs(7^2S_{1/2}) + Kr$ is a single, nondegenerate 7so state from which predissociation into states adiabatically separating into either $6^{2}P_{3/2}$, $5^{2}D_{3/2}$, or $5^{2}D_{5/2}$ seem precluded by available theoretical estimates^{17,18} of this molecular system. Separation into all three seems completely forbidden, adiabatically. Diabatic separation seems to be excluded by the strong dependence upon transition energy of the proportions of the products. Rather it appears that most of the features of Fig. 4 could be the result of the photolysis of Cs₂Kr, principally along the Cs-Cs bond. In such a system it would be reasonable to expect that the spectrum would resemble that of Cs_2 , red-shifted by the increasing potential found in the polarization energy of the more excited states, just as seen in Fig. 5. Such an identification would serve to explain all of the features of Fig. 4, except the red band leading to the production of $Cs(5^2D_{5/2})$ and the small peak labelled $6d\sigma$ already identified.

One of the differences between the bands of Fig. 4 attributed to Cs_2Kr and the corresponding spectrum³ of Cs_2 is the enhancement of the component of the blue band leading to $Cs(6\ ^2P_{3/2})$ relative to the components giving other products. This can be understood if it is assumed that the effect of attaching a Kr atom to Cs_2 is not so great as to seriously affect the order of the potential curves. In Cs_2 the small component of $Cs(6\ ^2P_{3/2})$ that



FIG. 4. Relative cross sections as functions of transition energies for selective photolysis of equilibrium populations of CsKr and Cs₂Kr into three of the lowest four energetically possible product states. Dashed and solid curves identify data for product states having j = 5/2 and 3/2, respectively. Error bars record representative scatter obtained during successive remeasurement, and the points marked A and B identify wavelengths useful in discussions.

results from photolysis at blue wavelengths was attributed³ to a weak predissociation by the strongly repulsive ${}^{3}\Sigma_{u}$ state correlated with $Cs(6 {}^{2}P_{3/2}) + Cs$ of the bound $E^{1}\Pi_{u}$ state excited directly by the absorption. The effect of a third body Kr atom might be to induce a greater mixing of the states resulting from $Cs_{2}(E^{1}\Pi_{u}) + Kr$ and $Cs_{2}({}^{3}\Sigma_{u}) + Kr$ and, hence, to cause a stronger predissociation.

The singular features appearing as lines in the spectra of Fig. 4 presented considerable difficulty in attempts at analysis. Those producing $Cs(6^{2}P_{3/2})$ corresponded in wavelengths to two doublets of atomic Cs, the allowed $6^{2}S \rightarrow 7^{2}P$ transition and the forbidden $6^{2}S \rightarrow 6^{2}D$. The lines producing $Cs(5^{2}D)$ corresponded to the former doublet. Data were difficult to obtain because absorption at the center frequencies by ground state Cs produced large populations of Cs(7P) and Cs(6D) which tended to saturate the detection system.²³ However, as shown in Fig. 4, excitation at wavelengths near to these

atomic lines did yield the products shown, although linearity of the system there was not certain. Detailed examination of those singular features lay beyond the scope of this work and it was not determined whether the products were obtained promptly from either or neither of Cs₂Kr or CsKr. However, it should be noted that similar features were observed^{2,3} in Cs₂ to result from photolysis excited from the lowest $Cs_2(^{3}\Sigma_{n})$ state by transitions to higher energy g states about which very little is known. Also, structures resembling lines were reported¹³ to result from the transitions $6so - 6d\delta$ and $6s\sigma - 6d\pi$ of CsKr at very large internuclear separations. These correlated with the forbidden $6^{2}S \rightarrow 6^{2}D$ transitions of atomic Cs. Either or both could contribute to the causes of the lines observed here, but the problem was not pursued further as the study of excited g states and levels excited in the visible spectrum that were capable of dissociating to states of Cs more energetic that $5^2 D_{5/2}$ proved too intractable to resolve with the data base available from this work. As described below, the



5D_{3/2}

6P3/2

The red band, reproduced in Fig. 6, is the feature most unequivocally attributable to photolysis of a parent CsKr molecule. It warrants several observations. Only the channel producing 5D is clearly the result of the photolysis of CsKr. The other channel, seen in Fig. 4, giving $6P_{3/2}$ at the red wavelengths is also most probably due to Cs₂Kr for the same reasons discussed above, as adiabatic separation of CsKr into $6P_{3/2}$ would be completely inexplicable at these transition energies. As in the case of $7s\sigma$, theory indicates that the $5d\sigma$ state to which this transition is generally attributed²⁰ is correlated adiabatically with a single limit $Cs(5^2D_{5/2}) + Kr$. The relatively small cross section shown in Fig. 4 for the component of photolysis producing $Cs(5^2D_{3/2})$ is seen to have the same structure as found in the major channel producing $C_{5}(5^{2}D_{5/2})$. To examine if this could be indicative of a secondary origin to the $Cs(5^2D_{3/2})$ fraction that arose from collisional mixing of the fine structure components of the Cs(5D) products, the relative cross sections were examined as functions of the delay between photolysis and detection.

Product state kinetics

To obtain values of delay between photolysis and detection that were comparable to the times which might be required for collisional mixing of the dissociation products, the photolysis step had to be excited by the auxiliary beam from the laser shown outside the dotted enclosure in Fig. 2. In this case the normal photolysis pulse was blocked and the detection step was delayed electronically, as shown in Fig. 2. The result is seen FIG. 5. Relative cross sections as functions of wavelength for selective photolysis leading to the production of Cs* atoms having J=3/2. Solid and dashed curves record cross sections for $Cs(6^2P_{3/2})$ and $Cs(5^2D_{3/2})$ products, respectively. Lightly drawn curves identify the results for Cs₂ obtained from Ref. 3, while heavy curves describe the results of this work attributed to Cs₂Kr. Only cross sections pertaining to the same parent molecule were plotted on the same relative scale.

in Fig. 7. The initially strong increase in the production of $5^2 D_{3/2}$ atoms with increased time of delay seems conclusive in indicating a secondary origin of that $5^2 D_{3/2}$ population. Moreover, the data of Fig. 7 implies there is no prompt source of $5^2 D_{3/2}$ atoms.

700.0

Superficially, the functional form of the dependence upon time appears to consist of the sum of two exponentials. This is to be expected if the populations of the two fine structure components were tightly coupled by collisional mixing, while being quenched more slowly at a common rate. Assuming transport to have been either negligible or identical for the populations N_5 and N_3 of the $5\,^2D_{5/2}$ and $5\,^2D_{3/2}$ levels, respectively, the kinetics



FIG. 6. Normalized cross sections as functions of wavelength for photolysis observed in the red region of the spectrum. The solid curve describes the photolysis of CsKr to produce $Cs(5\,^2D_{5/2})$ measured in this work through excitation of the transition $6s\sigma \rightarrow 5d\sigma$. The dotted curve shows the results reported in Ref. 20 that were obtained by detecting fluorescence indirectly produced from the various dissociation products.

4858

CROSS SECTION (rel.)

1.0



FIG. 7. Relative yields of the photolysis of CsKr at 632.5 nm as functions of the time elapsed between the arrival of the pulse used to induce photolysis and the pulse used to excite resulting products to Rydberg states for detection. Data points plot the experimental measurements of the $Cs(5^{2}D)$ product populations in each of the two fine structure states: +, $5^{2}D_{5/2}$; o, $5^{2}D_{3/2}$. Solid curves plot the best comparable estimates obtained from modeling the kinetics of the product state populations using rate coefficients described in the text. Dotted curves show sensitivity of the model to changes of a factor of 2 in the rate coefficient used to describe the mixing of the fine structure components.

modeling the following system:

$$Cs(5^{2}D_{5/2}) + Kr \frac{K_{d}}{K_{u}}Cs(5^{2}D_{3/2}) + Kr$$
, (3a)

$$\operatorname{Cs}(5^{2}D_{5/2,3/2})\left\{+\operatorname{Kr}\overset{Q}{\longrightarrow}\operatorname{Kr}\right\}+\operatorname{Cs}^{*},\qquad(3b)$$

where Q describes the composite rate for both collisional and radiative loss of 5^2D population, can be written

$$\frac{dN_5}{dt} = K_u N_3 - K_d N_5 - QN_5 , \qquad (4a)$$

$$\frac{dN_3}{dt} = -K_u N_3 + K_d N_5 - QN_3 , \qquad (4b)$$

with detailed balancing insuring that

$$K_d/K_u = N_{3e}/N_{5e} = (g_3/g_5) e^{i\Delta B i/kT}$$
 (4c)

In Eq. (4c) the subscript e denotes equilibrium values of population, the g represents statistical weights, ΔE the fine structure splitting in energy, and T the temperature.

The system of Eqs. (4a), (4b), and (4c) has the solutions

$$N_{5}(t) = N_{0}(1 + N_{3e}/N_{5e})^{-1}e^{-Qt} + N_{0}(N_{3e}/N_{5e})(1 + N_{3e}/N_{5e})^{-1}e^{-\nu t}$$
(5a)

$$N_{3}(t) = N_{0}(N_{3e}/N_{5e})(1 + N_{3e}/N_{5e})^{-1} (e^{-Qt} - e^{-\nu t}), \qquad (5b)$$

when the boundary conditions $N_5(0) = N_0$ and $N_3(0) = 0$ are imposed. In these solutions the relaxation frequency ν is $\nu = K_u + K_d + Q$. Since it can be reasonably assumed that $K_u + K_d \gg Q$, in the limiting case of long delay times $N_3(t)/N_5(t) - N_{3e}/N_{5e}$, which can be evaluated from Eq. (4c). Moreover, the comparison of the experimental ratio of the populations of the fine structure components at late times to the ratio computed from Eq. (4c) provides a direct means for verifying the values of the scaling parameter B_{rel} , used earlier to place the photolysis cross sections for the various products on the same relative scale. At the vapor temperature of 523 °K used in these experiments, the equilibrium ratio of Eq. (4c)has the value 0.87, which seems in good agreement with the ratio between the later time portions of the curves shown in Fig. 7. This appears to confirm the scaling procedure used through Eq. (2) to establish the scales of the data of Fig. 4, at least for the D states.

Also shown in Fig. 7 by the solid lines are the populations computed from Eqs. (5a), (5b), and (4c) which are in the best agreement with the data. The two adjustable parameters Q and K_d were given the values $Q = 2.1 \times 10^6$ sec⁻¹ and $K_d = 2.2 \times 10^7$ sec⁻¹. The effect of changes in Qis to change the late-time slope proportionally, while the sensitivity of the computations to changes in K_d of a factor of 2 have been explicitly shown in the figure. Using the tabulated^{24, 25} values for the radiative lifetimes of the 5D states, the rate coefficient for the collisional quenching of the $Cs(5^{2}D)$ population by Kr can be estimated to be $K_{5D} = 3.7 \pm 0.7 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$, while the rate coefficient for mixing of the fine structure populations produced by collisions with Kr can be estimated to be K_{d} $=7 \times 10^{-12}$ cm³ sec⁻¹ to within a factor of 2. The latter value is not inconsistent with mixing rates reported in the literature for selected states of various alkalis.²⁶ Of course, to obtain greater precision the destruction frequencies ν and Q should be measured over a range of partial pressures of cesium and krypton. Although such extensive measurements lay outside the scope of this work. the estimates reported above are interesting as an indication of the possibilities. The limits of uncertainty cited above were intended to reflect not only the scatter in the data but also to estimate the likely error introduced by neglecting to vary the parameter space in which the measurements were made.

The above considerations seem to confirm both qualitatively and quantitatively the interpretation that the photolysis band found in the red region of the spectrum of Fig. 4 yielding $5{}^{2}D_{5/2}$ products is the single $5d\sigma$ band correlated with $Cs(5{}^{2}D_{5/2}) + Kr$. The smaller band giving $5{}^{2}D_{3/2}$ products does so only because of subsequent collisional relaxation of the $5{}^{2}D_{5/2}$ dissociation product population directly produced from CsKr. Almost by elimination the photolysis band in the red region of the spectrum leading to $Cs(6{}^{2}P_{3/2})$ must result from a different parent molecule, and because of its similarity to a comparable structure in the spectrum of Cs_2 , it is proposed that the parent is Cs_2Kr .

As mentioned earlier, in experiments²⁰ in which the occurrence of photolysis was inferred from measure-

J. Chem. Phys., Vol. 75, No. 10, 15 November 1981

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.114.34.22 On: Fri. 28 Nov 2014 20:36:47



FIG. 8. Illustrative potential curves showing the asymptotic region of large separations for the constituents of Cs_2Kr at some arbitrary orientation that are useful in modeling the photolysis studies described in the text. The arrow marked 1 represents the transition excited by the photolysis pulse tuned to the wavelength denoted A in Fig. 4, while arrows marked 2 and 2' identity the transitions through which photolysis producting $Cs(5^{2}D_{5/2})$ occurs in the blue and red regions of the spectrum, respectively. The arrow marked 3 denotes a typical transition excited by the delayed pulse to raise the product state population into an easily detected Rydberg state Cs**.

ments of the fluorescence from some low transition such as (2') in Fig. 1, fed through cascading from the direct dissociation product, the resulting band would have been the composite of all bands from all parent molecules which could contribute population to the upper state radiating the transition (2'). From an inspection of Fig. 4 it becomes apparent that if detected through the time-integrated fluorescence of the transition $6^{2}P_{3/2}$ $-6^{2}S_{1/2}$, the red absorption band obtained for cesium krypton molecules would be the sum of the features shown in Fig. 4 for the production of $Cs(6^2P_{3/2})$ and $Cs(5^{2}D_{5/2})$, weighted in proportion to the distribution of population between the different initial molecular states. The result reported by Saver et al.²⁰ was obtained in this way and is plotted in Fig. 6 normalized together with the component $6s\sigma + 5d\sigma$ band from CsKr isolated in this work. It can be seen that the effect of including the relatively structureless $6P_{3/2}$ feature from Cs₂Kr is to reduce the contrast of the structure contributed by the CsKr band, as would be expected from Fig. 4. In this context it can be seen from Fig. 6 that the results of this work are in excellent agreement with the work of Sayer et al., 20 with present work representing a further improvement through removal of the contribution resulting from dissociation of some other parent molecule, probably Cs_2Kr , directly to $Cs(6^2P_{3/2})$.

DISCUSSION

The inference that the "other molecule" responsible for most of the features of the photolysis spectrum is Cs_2Kr is argued by the considerable similarity in the proportions of the various energetically possible products obtained in this work to those reported³ for the photolysis of Cs_2 . This similarity was shown in Fig. 5 for the yellow and green regions of the spectrum. One possible model explaining this similarity is seen in Fig. 8. There a schematic representation has been presented for important projections of the potential energy surfaces of Cs-Cs-Kr for some fixed relative orientation that is currently unknown. Along the Cs-Kr bond at a considerable distance from the other Cs atom the potential curves have been reproduced from Pascale and Vandeplanque.¹⁸ In the orthogonal direction along the Cs-Cs bond at a considerable distance from the Kr atom the potentials for Cs, have been reproduced³ with the excited states being lowered somewhat more by the greater energy lost in the polarization of the Cs_2^* -Kr pair. If this general relationship continued as the Cs_2^* -Kr distance were reduced, the spectrum of electronic transitions occurring over a reasonably large range of separations would resemble that of Cs_2 , but shifted to the red in a manner analogous to that observed for atoms in the presence of inert gases.

The results of the photolysis experiments could be explained within the context of Fig. 8 by considering the numbered arrows representing the various electronic transitions excited at the different wavelengths. As drawn, the arrow numbered 1 shows the effect of the photolysis pulse when tuned to the wavelength marked A in Fig. 4. It excites the state of the trimer correlated with $Cs_2(C^1\Pi_v) + Kr$, which should be significantly predissociated by the repulsive state $Cs_2(^{3}\Sigma_{\mu}) + Kr$ to give $Cs(6^{2}P_{3/2})$ if the pattern found³ in Cs_{2} is followed here. However, as seen in Fig. 4, the same wavelength does not excite the transition marked 2' in Fig. 8, which leads to the 5do state of CsKr dissociating to $Cs(5^2D)$. In a similar fashion the near-lying wavelength marked B in Fig. 4 should correspond to excitation of the state of the trimer correlated with $Cs_2({}^1\Sigma_y) + Kr$, also predissociated by $Cs_2({}^{3}\Sigma_{u}) + Kr$ to give $Cs(6 {}^{2}P_{3/2})$. Indications of the strength of the similarity between $Cs_2 + Kr$ and Cs_2 , as shown in Fig. 8, is found in the observation of the short wavelength edge to the production of $Cs(6^{2}P_{3/2})$ seen in the yellow band in Figs. 4 and 5. As described previously,³ this occurs for Cs₂ because of a competition between the predissociation by ${}^{5}\Sigma_{\mu}$ of the ${}^{1}\Sigma_{\mu}$ state excited in the yellow at a wavelength such as B in Fig. 4 and the direct dissociation of ${}^{1}\Sigma_{u}$ to $Cs(5 {}^{2}D_{5/2}) + Cs$ that becomes possible for transition energies exceeding 18055 cm⁻¹ that correspond to wavelengths shorter than 553.86 nm. The possiblity for dissociation of $Cs_2({}^1\Sigma_{\nu})$ excited at energies above that threshold so reduces the lifetime of the state that relatively little population remains long enough for predissociation to $Cs(6^{2}P_{3/2})$ to occur. A similar edge in these excimer spectra, red shifted as expected, is seen in Fig. 5. There the decrease in $6 {}^{3}P_{3/2}$ production and increase in $5 {}^{2}D_{5/2}$ production is quite noticeable as the transition energy is

As shown in Fig. 8, transition 1 acts to deplete the reservoir of parent population, here shown to be Cs₂Kr. Since the sample is optically thin at all visible wavelengths, the effect of a subsequent photolysis pulse exciting the same transition, or even some other transition such as the one marked 2 that would correspond to one of the blue bands causing dissociation to $Cs(5^2D)$, should be reduced in proportion to the amount of Cs₂Kr remaining. Conversely, the amount of the same product resulting from photolysis at some other wavelength exciting only the transition of CsKr marked 2' in Fig. 8 would be unaffected if the populations of CsKr and Cs2Kr were independent on the time scale of the experiment. However, the 10 Hz repetition rate employed in this experiment should have provided adequate time for the molecular fragments to reassemble between photolysis pulses.

At higher values of laser fluence it must be considered that the populations of Cs2Kr and CsKr are in a dynamic equilibrium. Continuous wave excitation of the vapor in this vellow and green region must be expected to disturb this equilibrium, perhaps significantly. Moreover, typical relaxation times for the dissociation products have been shown to be sufficient to provide the opportunity to integrate the illuminating intensity to a relatively large fluence. Thus, qualitatively the effect of cw illumination would be integrated to a level suggesting that in the examination of the yellow band previously identified¹⁹ as the 6sr-7so transition in CsKr, the steady state proportions of ground state CsKr and Cs2Kr parent molecules would have been considerably altered from the equilibrium value which would have existed in the absence of illumination. Conversely, since the intensity of the photolysis pulse in these experiments was always maintained at a value much below that demonstrated to cause nonlinear effects such as saturation, it could be concluded that the spectra of Figs. 4 and 5 represent the composite absorption spectra of the equilibrium distribution of population between the ground states of CsKr and Cs₂Kr. From this perspective it is not surprising that the vellow and green bands attributed in this experiment to Cs_2Kr do not closely resemble the previous results¹⁹ obtained with continuous-wave excitation. It might be argued that since the previous results in fact are different, those are the ones more nearly attributed purely to CsKr. If the composite rate for all of the kinetic steps necessary to reassemble the dissociation products into CsKr fortuitously exceeded that necessary to regenerate Cs_2Kr , then the equilibrium would have been shifted toward a predominance of CsKr in the presence of cw illumination. It appears this might have been the case since the reassembly of Cs2Kr would require the collision of two minor constitutents, either Cs + Cs or CsKr+ Cs, in addition to the many other steps in the kinetic sequence that should be roughly similar to those in the sequence producing CsKr. An examination of the spectrum in the yellow wavelength region as a function of the fluence of illumination at levels interpolating from those of this experiment to those used in the previous work¹⁹ should be able to show the continuous evolution

from the spectrum reported here to be characteristic of the intrinsic distribution of population between Cs₂Kr and CsKr to the form reported by Sayer et al.¹⁹ Further, such an experiment might be able to guide the extrapolation of the results to the asymptote characteristic of the absorption spectrum of CsKr in the absence of Cs₂Kr. It is consistent with the results observed here for the red $6s\sigma - 5d\sigma$ band to speculate that such an extrapolation would remove some residual absorption from Cs₂Kr probably present in the spectrum reported for $6s\sigma - 7s\sigma$. As shown in Fig. 6, the effect of the removal of the contribution from Cs₂Kr, somewhat masking the spectrum reported²⁰ for $6s\sigma - 5d\sigma$, was to improve the contrast of the small scale structure which might be useful in refinement of the theoretical estimates of the potential curves involved.

CONCLUSIONS

The first conclusion of this work is that to within what can be inferred about the differing equilibrium distributions of population between the ground states of Cs_2Kr and CsKr, the results of this work are in excellent agreement with the previous work of Sayer *et al.*^{19, 20} For the red band attributed to the $6s\sigma - 5d\sigma$ transition of CsKr, the present results represents a further improvement obtained through removal of the contribution resulting from photolysis of Cs_2Kr . The band reported here shows a higher contrast for the small scale structure which may be useful in the refinement of the potential curve for the $5d\sigma$ state.

The equilibrium distribution of ground state populations characteristic of this particular experiment was the intrinsic one corresponding to the kinetic equilibrium maintained in the limit of low intensities of illumination. This distribution favored Cs_2Kr to such an extent that all major features in the spectrum, other than $6s\sigma - 5d\sigma$ band, could be attributed to Cs_2Kr . In comparison with previous results, ^{19,20} it seemed that the kinetic equilibrium could be shifted in favor of CsKr, if the fluence illuminating the vapor in a time characteristic of the relaxation phenomena were sufficiently high, at least at longer wavelengths. In effect, it appears that the Cs_2Kr population could be, at least partially, "burned" out of the vapor.

The second major conclusion of this work is that the occurrence in the spectra of both Cs_2Kr and CsKr of relatively broad photolysis bands leading to extremely well-selected product states was a fairly common event. This continues the general phenomenology observed^{2,3} for Cs_2 . Again, here with CsKr and Cs_2Kr it appears that photolysis occurring at a transition energy not too much in excess of the threshold for the process leads to adiabatic and hence, state selective dissociation.

Finally, from the observations of the stability of the populations of the dissociation products against collisional mixing, conclusions can be drawn concerning the characteristic times over which state selective photolysis could be maintained. At least for the $Cs(5^2D)$ products, populations could be expected to remain in the same quantum state for tens of nanoseconds and in the same energy level, neglecting fine structure splitting, for a time of the order of 500 nsec. Quantitatively these

times correspond to rate coefficients of $K_d = 7 \times 10^{-12}$ $cm^3 sec^{-1}$ and $Q=3.7 \times 10^{-13} cm^3 sec^{-1}$ for fine structure mixing and for quenching of the $Cs(5^2D)$ states, respectively. The practical importance of this conclusion is that the time scale over which product populations could be photolytically pumped is defined. At this density, corresponding to a filling pressure for Kr of 100 Torr, the maximum fluence which could be applied to the production of populations of a single state would be equal to the illuminating intensity integrated over a few tens of nanoseconds. The fluence which could be used to populate a single energy level would be over an order of magnitude larger. Of course, more quantitative values could be obtained from refinement of the rate coefficients reported here. Qualitatively, such results demonstrating both highly selective but broad bands for photolysis, together with reasonable stability of product populations, appear very encouraging from the perspective of laser chemistry.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation in part by NSF Grant No. PHY 8019525 and in part by Grant No. INT 7618982 under the U.S. -Romanian Cooperative Program in Atomic and Plasma Physics.

¹C. B. Collins, J. A. Anderson, F. W. Lee, P. A. Vicharelli,

D. Popescu, and I. Popescu, Phys. Rev. Lett. 44, 139 (1980). ²C. B. Collins, J. A. Anderson, D. Popescu, and I. Popescu,

- J. Chem. Phys. 74, 1053 (1981).
- ³C. B. Collins, F. W. Lee, J. A. Anderson, P. A. Vicharelli, D. Popescu, and I. Popescu, J. Chem. Phys. 74, 1067 (1981).
- ⁴C. B. Collins, J. A. Anderson, F. W. Lee, P. A. Vicharelli,
 D. Popescu, and Iovitzu Popescu, in *Proceedings of the In-*
- ternational Conference on Lasers 1979, edited by V. J. Corcoran (STS Press, McLean, Va, 1980), pp. 185-189.
- ⁵H. Hoffman and S. R. Leone, J. Chem. Phys. 69, 381 (1978).
- ⁶J. Maya, IEEE J. Quantum Electron. 15, 579 (1979).
- ⁷A review of work prior to 1957 is found in S. Ch'en and M.

Takeo, Rev. Mod. Phys. 29, 20 (1957).

- ⁸The transition of concepts is presented by C. L. Chen and A. V. Phelps, Phys. Rev. A 7, 470 (1973), and in references cited therein.
- ⁹F. Besombes, J. Granier, and R. Granier, Opt. Commun. 1, 161 (1969).
- ¹⁰J. Granier and R. Granier, J. Quant. Spectrosc. Radiat. Transfer **13**, 473 (1973).
- ¹¹W. Happer, G. Moe, and A. C. Tam, Phys. Lett. A 54, 405 (1975).
- ¹²G. Moe, A. C. Tam, and W. Happer, Phys. Rev. A 14, 349 (1976).
- ¹³M. A. Chellehmalzadeh and C. B. Collins, Phys. Rev. A 19, 2270 (1979).
- ¹⁴A. Tam, G. Moe, W. Park, and W. Happer, Phys. Rev. Lett. **35**, 85 (1975).
- ¹⁵B. Sayer, M. Ferray, J. Lozingot, and J. Berlande, J. Phys. B 9, L293 (1976).
- ¹⁶A. C. Tam and G. W. Moe, Phys. Rev. A 14, 528 (1976).
- ¹⁷J. Pascale and J. Vandeplanque, J. Chem. Phys. **60**, 2278 (1974).
- ¹⁸J. Pascale and J. Vandeplanque, Centre d'Etudes Nucléaires-Saclay, Service de Physique Atomique Commissariat à l'Energie Atomique Report, 1974 (unpublished).
- ¹⁹B. Sayer, M. Ferray, and J. Lozingot, J. Phys. B **12**, 227 (1979).
- ²⁰B. Sayer, M. Ferray, J. P. Visticot, and J. Lozingot, J. Phys. B **13**, 177 (1980).
- ²¹E. Czuchaj and J. Sienkiewicz, Z. Naturforsch. Teil A 34, 694 (1979).
- ²²K. Niemax, J. Phys. B 13, 1791 (1980).
- ²³D. Popescu, M. L. Pascu, B. C. Collins, B. W. Johnson, and I. Popescu, Phys. Rev. A 8, 1666 (1973).
- ²⁴M. Fabry, J. Quant. Spectrosc. Radiat. Transfer 16, 127 (1976).
- ²⁵A. Lindgard and S. E. Nielsen, At. Data Nucl. Data Tables 19, 533 (1977).
- ²⁶ The value reported here corresponds to a cross section of 1.5 Å^2 which falls reasonably between the hundreds of \AA^2 reported by A. C. Tam, T. Yabuzaki, S. M. Curry, M. Hou, and W. Happer, Phys. Rev. A 17, 1862 (1978) for Rydberg states with more closely spaced fine structure components and values around 10⁻⁴ Å obtained by E. E. Nikitin, in *The Excited State in Chemical Physics*, edited by J. Wm. McGown. (Wiley, New York, 1975), pp. 317–377, for the mixing of the lowest P states having fine structure intervals considerably exceeding that of Cs(5²D).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP