Multiphoton ionization of cesium through resonant dissociative states of Cs_2†

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(Received 10 December 1973)

The multiphoton excitation of cesium through potentially resonant continuum molecular states is investigated over the 6200–5000-Å wavelength region with a tunable dye-laser source having a 0.06–0.08-Å linewidth and a space-charge ionization detector sensitive to a few ions per second. Conditions are established under which the lifetime of the resonant intermediate state against photoexcitation exceeds the lifetime against dissociation. Single- and double-photon resonances occur for the same wavelength and give absorption maxima corresponding to the line spectrum from the intermediate state following dissociation. These lines are modulated in amplitude as a function of wavelength by the more slowly varying absorption resonance from the initial to the intermediate continuum state. As a consequence, the resulting dispersion curve for two-photon absorption in cesium shows what appear to be resonant intermediate $d\pi(^3\Pi_g)$ terms dissociating to give a 5^2D atom and resulting in the strong development of features corresponding to the fundamental series ($5^2D \rightarrow n^2F$) of atomic cesium in absorption. Components to $n = 50$ were observed and recorded to a precision sufficient to determine the average quantum defect for F states to be $\langle n - n^* \rangle = 0.033$ in the limit of large n. More complex structure is attributed to $p\pi(^3\Pi_g)$ and $p\sigma(^1\Sigma_u)$ terms dissociating to give a $6\,^2P_{3/2}$ atom and resulting in the development of the $n = 8$ to 32 components of the $6\,^2P_{3/2} \rightarrow n^2D_{3/2,5/2}$ part of the diffuse series in absorption. Terms dissociating into $6\,^2P_{1/2}$ were found only at higher photon energies (~2.27 eV) corresponding to the $n \geq 10$ members of the $6\,^2P_{1/2} \rightarrow n^2D_{3/2}$ series.

I. INTRODUCTION

The importance of molecular components to the multiphoton ionization of cesium has been discussed in recent letters[1,2] and communications.[3] It has been demonstrated[3] that the possibility of resonant intermediate states of Cs_2 can cause the dispersion spectrum for ionization to be completely dominated by structure corresponding to molecular absorption bands, even at rather low molecular-to-atomic ratios. This paper reports the extension of these results to the investigation of multiphoton excitation of cesium through potentially resonant continuum molecular states resulting from collisions of the excited atoms.

The inclusion of collision states into the scheme of multiphoton excitation of cesium in the visible-wavelength range, in a sense, represents a generalization of three-photon ionization models originally formulated for isolated cesium atoms.[4,5] For a single ground-state atom in the appropriate dipole approximation, expressions for the line strength for multiphoton excitation and ionization contain products of terms of the form

$$T_1(p_i, s) = \frac{\langle p_i | z | s \rangle}{E_i - E_0 - h\nu} \tag{1a}$$

and

$$T_2(l_j, p_i) = \frac{\langle l_j | z | p_i \rangle}{(E_j - E_i) + (E_i - E_0) - 2h\nu}, \tag{1b}$$

where the matrix elements are the usual dipole values with summations implied over products of intermediate-state quantum numbers not explicitly expressed. Values of l can be either s or d in accordance with dipole selection rules, and the first intermediate state must be a p_i as indicated. As has been discussed, dispersion curves for processes depending on line strengths containing such terms can be expected to be dominated by single-photon resonances arising from zeros in the denominators of the T_1 terms of Eq. (1a), two-photon resonances from the T_2 terms of (1b), and higher-order resonances where appropriate. Examples of the two-photon resonances of (1b) have been recently reported[6] for both $l_j = j^2S_{1/2}$ and $l_j = j^2D_{3/2,5/2}$.

For nonisolated atoms, the occurrence of molecular continuum states resulting from binary col-

lisions must be considered, and the resonances of (1a) and (1b) can be expressed

$$T_1(\psi(p_i),\psi(s))=\frac{\langle\psi(p_i)|z|\psi(s)\rangle}{E_i(R_1)-E_0(R_1)-h\nu} \tag{2a}$$

and

$$T_2(\psi(l_j),\psi(p_i))$$

$$=\frac{\langle\psi(l_j)|z|\psi(p_i)\rangle}{[E_j(R_2)-E_i(R_2)]+[E_i(R_1)-E_0(R_1)]-2h\nu}, \tag{2b}$$

where now $\psi(l)$ is one of the manifold of molecular states dissociating into l. Dispersion forces can be expected to remove the degeneracies between many of these states, and the energy of the transition, of course, becomes a function of R, the internuclear separation of the colliding pair. In the case of sufficiently repulsive potentials, the internuclear separation can change during the lifetime of the intermediate state, as implied in (2b). The resulting line strength must then be integrated over distributions of R. It is the modifications of the dispersion curve for multiphoton excitation which are implied by Eqs. (2a) and (2b) that are the concern of the experiment reported here. Because of the possible occurrence of strongly repulsive potentials with considerable variation over the possible values of R, there is the possibility of obtaining simultaneous resonances in both single-and double-photon terms. In particular, for those R for which

$$E_j(R_2)-E_i(R_2)=h\nu=E_i(R_1)-E_0(R_1), \tag{3}$$

strong double resonances should be observed in the spectra of the yield of the final state, provided overlap integrals implied in the matrix elements do not preclude transitions at those R.

The examination in this work of the dispersion spectrum for the ionization of cesium with a tunable dye laser in the 6200–5000- Å region has led to the identification of two photon-absorption transitions through what appear to be intermediate $d\pi(^3\Pi_g)$ terms that dissociate to give a $5\,^2D$ atom and result in the strong development of features corresponding to the fundamental ($5\,^2D \rightarrow n\,^2F$) series of atomic cesium in absorption. Components to $n=50$ were observed and recorded to a precision sufficient to extend existing tabulations of $n\,^2F$ term values beyond the previous limits of $n=14$ obtained from classical emission spectra[7] and $n=23$ from absorption.[8]

More complex structure in the spectrum for multiphoton excitation evidently results from $p\pi(^3\Pi_g)$ and $p\sigma(^1\Sigma_u)$ terms which are potentially resonant and dissociate into a $6\,^2P_{3/2}$ together with a $6\,^2S_{1/2}$ ground-state atom. Linewidth of the dye laser has been adequate to resolve both splitting of the intermediate $6\,^2P_{3/2}$ and the broadening of the resulting transitions caused by the molecular interactions. Terms dissociating into a $6\,^2P_{1/2}$ atom have been found at substantially higher photon energies around 2.27 eV.

The results of this work are believed not only to indicate the importance of dissociative molecular states to the multiphoton ionization of cesium at wavelengths below 6200 Å, but also to point toward the development of techniques for the correlation of continuum molecular states observed in absorption with the resulting dissociation products.

II. THEORY AND EXPERIMENTAL METHOD

For illustration, Fig. 1 presents one possible estimate of the location of the more important molecular potentials of cesium not inconsistent with previous spectroscopic studies,[9,10] theoretical

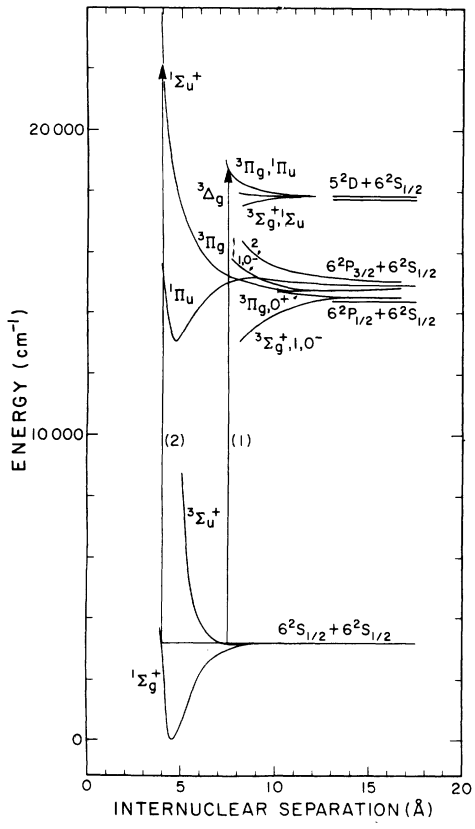

FIG. 1. Illustrative potential curves for the energy in cm^{-1} of Cs* + Cs as a function of internuclear separation. Only molecular states optically connected to one of the states originating from Cs($6\,^2S$) + Cs($6\,^2S$) are shown. An absorption transition occurring at the large internuclear separation characteristic of the $^3\Sigma_u^+$ state and leading to dissociation is indicated by arrow (1), while a similar transition from the smaller-R characteristic of the $^1\Sigma_g^+$ state is shown by arrow (2).

calculations,[11,12] and the results of this work to be discussed. Not shown are potentials for states forbidden to optical transitions from both states resulting from two $6\,^2S$ atoms by either strong (case c) or approximate (case a and b) selection rules. Such states would not be expected to yield T_1 terms in the dipole approximation.

Both a $^1\Sigma_g^+$ and a $^3\Sigma_u^+$ can arise from the collision of two $6\,^2S_{1/2}$ ground-state atoms. The former is strongly bound and forms the ground state of the Cs_2 molecule with a dissociation energy[10] of 3197 cm^{-1}. The triplet state is repulsive with a small van der Waals minimum[13] of the order of 50 cm^{-1} around 7–8 Å. Depending upon the height of possible centrifugal barriers, equilibrium populations of both states could be expected to be of the order of 10^3–10^5 cm^{-3} for energies within a few kT of that of an isolated $6\,^2S$ atom and at a pressure of 0.1 Torr of cesium vapor. For comparison, the equilibrium population at the bottom of the potential well of the $^1\Sigma_g^+$ state is around 8×10^{12} cm^{-3} at 500 °K.

Thus, transitions of the T_1 type could occur for three possible populations and internuclear separations; the strongly bound Cs_2 population of the $^1\Sigma_g^+$ at R around 4.5 Å, the population of the vibrationally excited levels of the $^1\Sigma_g^+$ state within a few kT of the dissociation limit at internuclear separations in the 4–7 Å range, and the population of the $^3\Sigma_u^+$ van der Waals state at $R \geq 7$ Å. Although $6\,^2S_{1/2} \rightarrow 5\,^2D_{5/2,3/2}$ transitions are forbidden in absorption in the dipole approximation and cannot contribute to T_1 terms in the limit of $R \rightarrow \infty$, several possibilities occur for transitions between molecular states resulting from the pair. One possibility, the $s\sigma(^3\Sigma_u^+) \rightarrow d\pi(^3\Pi_g^+)$, is indicated by the arrow marked (1) in Fig. 1. Depending upon the relative steepness of the upper and lower potential curves, absorption to the $d\pi(^3\Pi_g)$ state could be expected to span a range of photon energies lying to the violet of the threshold at 6851 Å corresponding to the energy difference of the $6\,^2S$ and $5\,^2D$ parent atoms.

For a strongly repulsive state, dissociation would occur within the lifetime of the intermediate state and the transition caused by the "second photon" should correspond to a component of the absorption spectrum of an isolated $5\,^2D$ atom. If the photon energy also corresponds to such a component, then both a T_1 and T_2 resonance would occur with a resulting high yield of final states.

Similar possibilities occur for excitation from both the strongly and weakly bound populations of the $^1\Sigma_g^+$ state with the restriction that the intermediate state now be of u symmetry. The arrow marked (2) in Fig. 1 indicates a possibility for excitation of the $^1\Sigma_u^+$ state from levels high in the well of the $^1\Sigma_g^+$ state. It should be noted that the absence of a molecular band observed either in absorption or emission which could correspond to a transition between these two states together with the estimates of Mulliken[11] that $^1\Sigma_u$ lies above $^3\Pi_u$ argues for the repulsive nature assigned to the $^1\Sigma_u$ in the figure.

The principal differences in the three possible initial states for multiphoton transitions lie in the different internuclear separations at which such transitions could be expected, as already discussed, and in the energy threshold for each. Table I summarizes the long-wavelength limit for single-photon resonances to the three principal manifolds of states resulting from the $6\,^2P_{1/2}$, $6\,^2P_{3/2}$, and $5\,^2D_{3/2,5/2}$ levels of the separated atoms at internuclear separations sufficient to ensure that dissociation can occur.

The $6\,^2P_{1/2}$ and $6\,^2P_{3/2}$ levels are treated separately because the occurrence[12] of large R^{-3} resonant van der Waals forces together with a significant doublet separation and the paucity of states resulting from the $6\,^2P_{1/2}$ level suggest *a priori* differences in the occurrence of the two as intermediate states. Such resonant dispersion forces characterizing S-P collisions complicate considerably the correlation of molecular terms with collision states arising from $6\,^2P$ atoms by introducing potential crossings at large internuclear separations, 12–14 Å. On the basis of these crossings, which are presumably avoided in a type-c coupling scheme, together with theoretical guidance from analogous problems,[11,12] the most probable correlation appears to be that, for the u states, only $^3\Pi_{u1,0^-,0^+}$ arise from $6\,^2P_{1/2}$ and for the g states, only $^3\Pi_{g0^+}$ and $^3\Sigma_{g1,0^-}$. All the u states dissociating into $P_{1/2}$ atoms which could serve as intermediate states for excitation of $^1\Sigma_g^+$ state populations are triplets and therefore forbidden to dipole transitions in case-a or case-b couplings which could be expected at the smaller internuclear separations characteristic of those initial states. Of the g states which could be excited, the $^3\Sigma_g$, $\Omega = 1$, and 0^- have strongly attractive van der

TABLE I. Long-wavelength limits for single-photon resonances to intermediate states dissociating to $6\,^2P_{1/2}$, $6\,^2P_{3/2}$, and $5\,^2D_{3/2,5/2}$ atoms from the three principal initial states together with most probable internuclear separations for the first resonance.

Initial state	Characteristic R	Long-wavelength limits for states dissociating to $6\,^2P_{1/2}$	$6\,^2P_{3/2}$	$5\,^2D_{5/2}$
$^3\Sigma_u^+$	7–8 Å	8945 Å	8523 Å	6851 Å
$^1\Sigma_g^+ (v \rightarrow \infty)$	4–7 Å	8945 Å	8523 Å	6851 Å
$^1\Sigma_g^+ (v = 0)$	4.5 Å	6956 Å	6698 Å	5620 Å

Waals forces,[12] and so would be resonant only to the red of the 8945 -Å limit shown in Table I, even at the minimal separation of the $^3\Sigma_g^+$ initial state that could be significantly populated. The remaining $^3\Pi_{g0^+}$ state has polarization difficulties when the quantization of Ω in case c along the direction of the E field of the laser radiation is considered. Of the resulting Stark components from the ground state, only the $M_\Omega = 0$ resulting from $\Omega = 1$ should be able to combine with 0^+ of the upper state and this is in violation of $0 \rightarrow 0$ selection rules, assuming no change of the weakly coupled rotational motion of the collision state. Consequently, excitation of intermediate $6\,^2P_{1/2}$ atomic states is *a priori* expected to occur with greater difficulty and probably only as a consequence of higher-order effects such as excitation and predissociation of states resulting originally from d terms and requiring higher-energy threshold photons than for $6\,^2P_{3/2}$.

In contrast, excitation of the $6\,^2P_{3/2}$ intermediate state does not present such problems because of the greater number of potential terms arising from $6\,^2P_{3/2} + 6\,^2S_{1/2}$ and being suitably repulsive in character. Sufficient terms are available for excitation from either $^1\Sigma_g^+$ or $^3\Sigma_u^+$ initial states.

The experimental method used in this and related works is based upon the detection of ionization resulting from the chemistry of the excited states populated by the absorption event. Useful detecting sequences have been found to include multiphoton ionization, associative ionization, and electron-impact ionization by thermal electrons of low energy. The positive ions produced in this way enhance the output signal of a thermionic diode containing the absorbing gas by partially neutralizing the negative space charge surrounding the diode filament. The relatively longer time the positive ions spend traversing the potential well of the space-charge region provides for the release of 10^4–10^6 electrons per ion from that region. Further amplification of 10^4–10^5 is provided externally by a tuned amplifier as previously discussed.[6] Essentially, this technique when coupled with excitation from a tunable dye laser and computer-interfaced detection as shown in Fig. 2 represents a modernization of the early experiments on photoionization.[14–17] These techniques are now sufficient to allow detection of ion signals as small as a few per second.

The particular absorption cell used in these studies was of Pyrex glass with quartz windows and filled with cesium at a pressure controlled by a two-chamber oven. The detecting diode included in the cell consisted of a 0.15-mm-diam tungsten-wire filament and a silver-disk anode, both activated with cesium and separated by 1.5 mm. They were aligned so that the diode-conduction path lay transverse to the optical axis.

The photon source was a tunable dye laser constructed from standard components as shown schematically in Fig. 2. It was operated in the pulsed mode and pumped with a nitrogen laser delivering about 50 kW peak power to the dye. Pulse widths were of the order of 15 nsec, and repetition rates were 8 sec^{-1} as limited by drift times for ions within the space-charge diode. The dye laser was operated with a rhodamine 6G, B, and HCl mixture and continuously tuned with 0.18-cm^{-1} bandwidth through the 5750–6200-Å wavelength range and

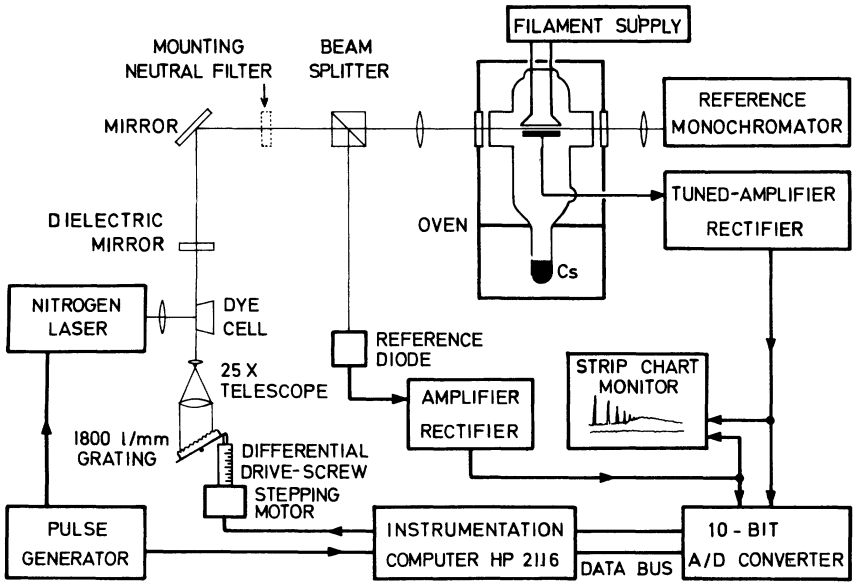

FIG. 2. Schematic representation of the arrangement of the tunable dye laser, cesium absorption cell with included detector diode, and data acquisition electronics used in these experiments.

with a 4-methylumbelliferone, fluorescene, and HCl mixture in the shorter-wavelength range to 5000 Å. The output beam was focused into the absorption cell, and the exact position of the focal volume within the detecting diode structure was not found to be particularly critical. It was only required that the positive ions ultimately produced from the products of the absorption process under investigation be able to diffuse or drift into the space-charge cloud surrounding the heated filament. Satisfactory signal-to-noise performance was found for a working pressure corresponding to a saturated vapor of 490 °K. Under these conditions, the number density of cesium atoms was 3.1×10^{15} cm^{-3}, while that of the molecular cesium, Cs_2, was 7.8×10^{12} cm^{-3}. Optional-filament temperatures were of the order of 1100 °K for the detecting diode.

As the laser output was not of constant intensity either as a function of time or wavelength, it was found necessary to simultaneously digitize both the diode output signal resulting from the photon absorptions and the input laser intensity for each laser pulse. This was accomplished as shown in Fig. 2 with a 10- bit A/D conversion system directly interfaced to an appropriate instrumentation computer. It additionally supplied the pulse train necessary to advance the laser wavelength in 0.03-Å steps after the proper sampling time had elapsed. Linearity of the wavelength drive was monitored with a 6-mm etalon which produced intensity modulations detected in the data channel used to record the laser-input intensity.

III. RESULTS AND CONCLUSIONS

A. Resonances from fundamental series, $5^2D\rightarrow n^2F$

Most pronounced in the spectrum in the wavelength region under observation was a strong development of structure corresponding to components of the fundamental series of atomic cesium. It was found together with underlying structure from the cesium molecular band at 6250 Å, resulting from the two-photon photoionization of ground-state Cs_2, as discussed previously.[3]

The resulting ion current corresponding to the relative probability of photoabsorption is shown as a function of wavelength in Figs. 3(a) and 3(b). The variation in input laser intensity is shown below the diode signal for reference. The pronounced structure corresponds, as marked, to the cesium $5^2D_{3/2}$–$n^2F_{5/2}$ series convergent at 5912.99 Å and the $5^2D_{5/2}$–$n^2F_{7/2,5/2}$ convergent at 5947.32 Å with components clearly identifiable from $n=12$ to $n\simeq 50$. Irregularities in the spacing of successive series members is an artifact of the drive mechanism of the laser grating and can be corrected, as mentioned above, from the intensity modulation

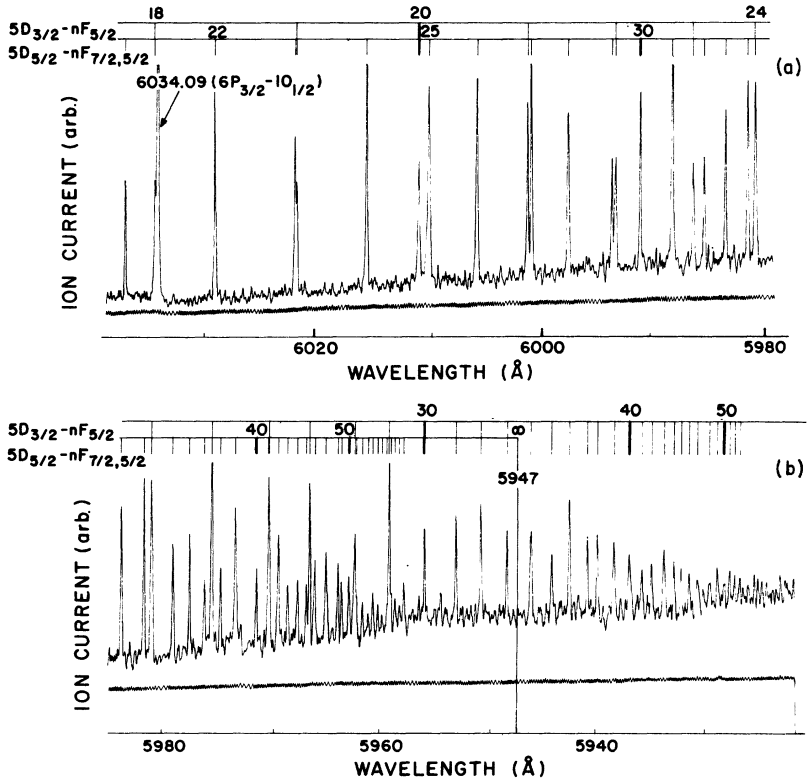

FIG. 3. Upper curve: photoionization spectrum as a function of wavelength. The large signals correspond to sequences of the fundamental series arising from absorption transitions from the $5^2D_{3/2,5/2}$ states to the $n^2F_{5/2,7/2}$ states. Above each curve is indicated the principal quantum number, n, of the corresponding line. Lower curve: input laser intensity as a function of wavelength showing the intensity modulation introduced by the 6-mm external etalon for the purposes of calibrating the wavelength linearity; (a) Upper spectrum: wavelength region 6040–5980 Å, and (b) Lower spectrum: wavelength region 5980–5920 Å.

imposed by the 6-mm etalon and seen in the lower trace of Fig. 3. The lowest-energy F level which could be excited was $8F$ which corresponds to a long-wavelength limit for the threshold for production of $5\,^2D$ atoms of at least 6628.66 Å.

Tabulation and correction of the data of Figs. 3 was used to derive effective principal quantum numbers, n^*, for the F states. Averaging to improve experimental statistics yielded an average limiting quantum defect for the F states of

$$\langle n - n^* \rangle = 0.033 . \quad (4)$$

Also of interest is the average value of the doublet separation derived for the two series to the $5\,^2D_{5/2}$ and $5\,^2D_{3/2}$ levels. From this was determined an experimentally averaged level splitting for the $5D$ level of

$$\Delta\nu_D = 97.59\ \text{cm}^{-1}, \quad (5)$$

which is in agreement with previous values[7,18] of 97.589 and 97.5884 cm^{-1}.

Although large populations of lower-lying excited states have been observed in fluorescence from cold cesium vapor excited by a continuous argon-ion laser and attributed to the result of complex excited-state chemical mechanisms, it is unlikely those reactions are relevant to this experiment. In the pulsed-laser experiment reported here, the duration of the absorbed photon pulse is about four orders of magnitude less than the inverse collision frequency and effectively precludes any appreciable excitation transfer between cesium species during the time the fundamental series could be excited. Conversely, the repetition rate for the laser is orders of magnitude slower than the destruction frequency for excited species produced by preceding pulses so that the production of $5\,^2D$ atoms and the subsequent transitions to the $n\,^2F_{5/2,7/2}$ states must occur within the same 10^{-8}-sec interval.

The existence of an appreciable, 0.2 Å^2, absorption cross section, experimentally observed[19] for cesium in the 5700–6000-Å wavelength region qualitatively suggests the availability of continuum states having suitable energies at internuclear separations of significance for T_1 resonances. That the energy threshold lies considerably lower than the minimum listed in Table I as required for excitation of the large $^1\Sigma_g$ ground-state population, implies that either or both of the collision state populations of $^1\Sigma_g^+$ and $^3\Sigma_u^+$ are those initially excited by the T_1 resonance. Since the populations of both states are considerably less than that of the ground $^1\Sigma_g^+$, saturation of the ionization yield of the multiphoton processes could be expected at considerably lower laser intensities. This is clearly found to be the case. Figures 4(a) and 4(b) present the data obtained from examination of the ion-current yield in the two cases as a function of the laser intensity. Intensity ranges, while not standardized absolutely, are similar in the two figures.

Figure 4(a) records the ion yield at 5988 Å corresponding to the T_2 resonance for the transition $5\,^2D_{5/2} \rightarrow 31\,^2F_{7/2,5/2}$. A clear second-order dependence is seen for the line intensity as indicated at lower intensities and almost complete saturation at the highest intensity. Analogous data for the background ion current obtained from limits of the continuum lying immediately adjacent to the sides

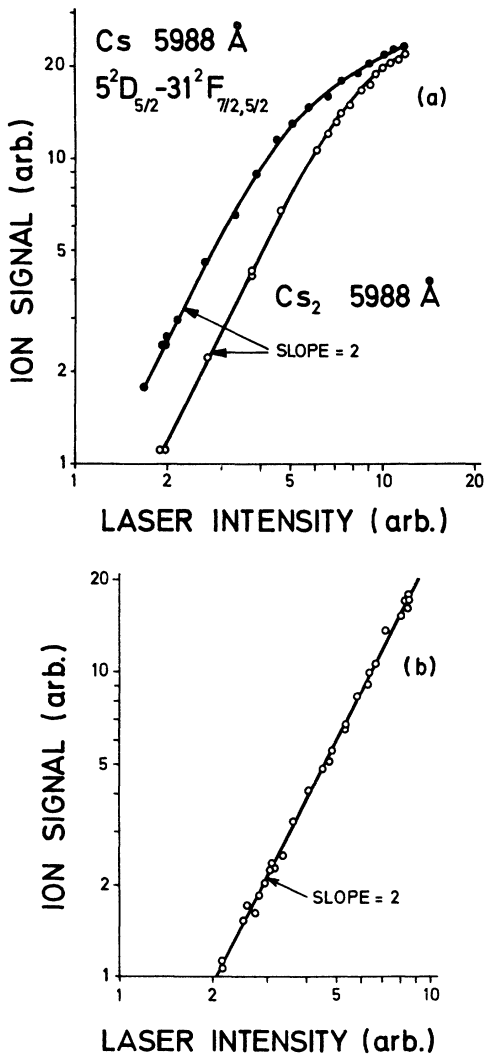

FIG. 4. Photoionization current less dark current as a function of laser intensity; (a) ●, ion signals corresponding to the peak of the $5^2D_{5/2}$–$31^2F_{7/2,5/2}$ line at 5988 Å; ○, ion signals corresponding to the limits of the continuum lying immediately adjacent to the sides of the 5988-Å line. (b) ion signal corresponding to the (19, 12) v'', v' component of the $X \rightarrow C$ transition at 6440.2 Å for two-photon ionization of Cs_2.

of the line are presented in Fig. 4(a) and are seen to have the same dependence as the resonance line. This could be expected to occur from a blurring of the resonance as a result of variation in R_2 in Eqs. (2b) and (3) during the transition from the intermediate state.

Figure 4(b) presents for comparison the ionization yield as a function of laser intensity which was reported previously,[3] for the (19, 12) component of the T_1 resonance at 6440.2 Å for two-photon ionization of the component of the bound $^1\Sigma_g^+$ population having $v''=19$. No evidence of saturation is seen and the dependence is clearly quadratic as would be expected from the relatively larger population of that initial state.

The most probable excitation sequence appears to include absorption first through a T_1 resonance to a $d\pi$ or $d\sigma$ intermediate state from either or both of the $^1\Sigma_g^+(v\to\infty)$ or $^3\Sigma_u^+$ collision states according to

$$Cs_2^{**}(^3\Sigma_u^+)+h\nu\to Cs_2^{**}(d\pi\,^3\Pi_g), \tag{6a}$$

$$Cs_2^{**}(^1\Sigma_g^+)+h\nu\to Cs_2^{**}(d\pi\,^1\Pi_u), \tag{6b}$$

where the double asterisk indicates a continuum state. In the first case, $d\pi(\Pi_g)$ is preferred over $d\sigma(\Sigma_g)$ by analogy with the p terms for which Π_g lies above Σ_g, the latter having little repulsive character at the large internuclear separation characteristic of $s\sigma(^3\Sigma_u^+)$. However, for the d states the dispersion forces are nonresonant, hence of a R^{-6} nature, and at the large R may not provide the span of energies over which the double resonance was observed, particularly for the $d\sigma(\Sigma_g)$ state, presumed attractive. In the second case, $d\pi(\Pi_u)$ is preferred over $d\sigma(\Sigma_u)$ for the same reasons, although the much smaller characteristic R makes this preference doubtful. Since the $d\pi(^1\Pi_u)$ is most probably the bound C state suggested by Kusch and Hessel,[9] to dissociate to a $5D$ atom, the transition must occur for the smallest R's corresponding to turning points in the $^1\Sigma_g^+$ state to give population of $d\pi(^1\Pi_u)$ lying above the dissociation limit.

The second excitation step should occur from the T_2 resonance following dissociation of the intermediate state,

$$Cs_2^{**}(d\pi)\to Cs(5\,^2D)+Cs, \tag{7}$$

by absorption of a second photon

$$Cs(5\,^2D)+h\nu\to Cs(n\,^2F). \tag{8}$$

Subsequent detection could be expected through an ionizing step which at lower laser intensities need not occur during the 10^{-8}-sec period of illumination. The ionizing step can be either

$$Cs(n^2F)+Cs\to Cs_2^+ +e \tag{9a}$$

or

$$Cs(n^2F)+Cs\to Cs^+ +Cs^-. \tag{9b}$$

According to Lee and Mahan[20] associative ionization by reaction (9a) is the dominant reaction channel for ionization of P states having $n\leq 12$, while (9b) becomes of primary importance for $n>12$. While the analogous determination of ionization products resulting from F states has not been made, it appears probable that their reactions would be similar to those of P states of comparable energy. In the case of the spectra observed in this work and presented in Fig. 3, only transition to high levels with $n>12$ were examined in detail which implies ionization occurred primarily according to (9b).

In the case of this excitation sequence, it could be reasonably expected that there would be evidence of a superimposed amplitude modulation of the components of the fundamental series as a function of wavelength resulting from the more slowly varying T_1 resonance for reactions (6a) and (6b). Such variations are in fact seen in the data of Figs. 3 as an envelope to the Rydberg-like spectrum of the fundamental series.

These results suggest the use of two synchronized excitation sources of different wavelength in which one remains fixed to detect the dissociation products through the T_2 resonances from step (8). The other would be varied in wavelength to probe the structure of the repulsive parts of the states excited by the T_1 resonances according to Eqs. (6a) and (6b).

B. Resonances from diffuse series, $6^2P_{1/2,3/2}\to n^2D$

As inferred in Sec. II, in addition to structure in the photoionization spectrum corresponding to the fundamental series, parts of the diffuse series were obtained. Of particular interest was the much higher photon energy required to excite lines from the $6^2P_{1/2}$ level than for the $6^2P_{3/2}$.

Three features were observed. The strongest were components corresponding to the $n=8$–10 members of the $6^2P_{3/2}\to n^2D_{3/2,5/2}$ doublet of the diffuse series, substantially split and broadened as typified by the $6^2P_{3/2}\to 9^2D_{3/2,5/2}$ structure at 5847 Å shown in Fig. 5. Of secondary importance were higher members of the same series to $n=32$, not noticeably broadened. The third type of feature comprised members of the $6^2P_{1/2}\to n^2D_{3/2}$ part of the diffuse series, but only for $n\geq 10$. Components for $n=7$–9 could have been expected in spectral regions relatively unobscured by other structure, but were not observed for any of the laser intensities available to this experiment. The nonoccurrence of transitions from the $6^2P_{1/2}$ level at lon-

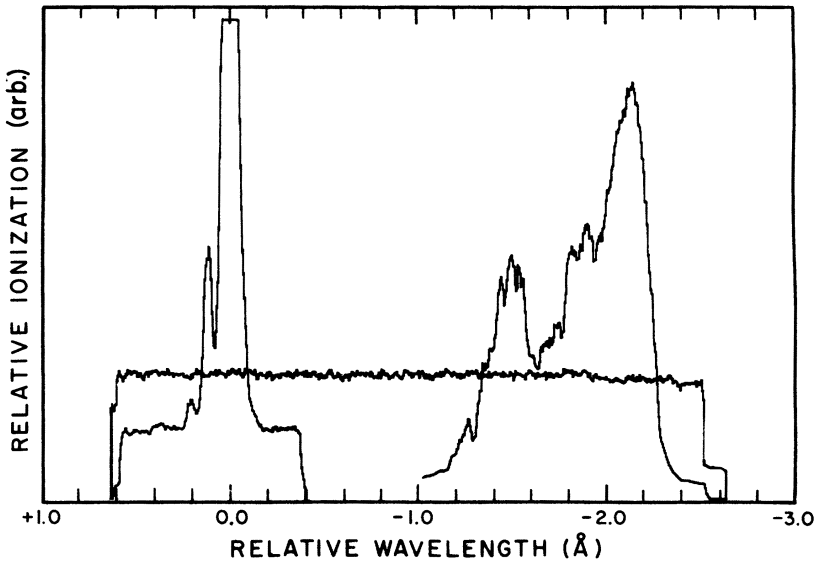

FIG. 5. Direct recording of the detected ion current (upper curve), and input laser intensity (lower curve), as functions of wavelength for the 2-Å interval containing the $6\,^2P_{3/2} \rightarrow 9\,^2D_{3/2}$ transition (left-hand-side curve); and the 2-Å interval containing the $6\,^2P_{3/2} \rightarrow 9\,^2D_{5/2}$ transition (right-hand-side curve). Amplifier gain differs for the two traces.

ger wavelength is the most unequivocal indication that no significant component of intermediate-state population of atomic cesium results from processes other than photon absorption.

Both of the last two classes of excitations appeared first at long-wavelength limits below 5600 Å, approximately the limit shown in Table I for the excitation of dissociative d terms from either of the two ground collision states. This strongly suggests that at wavelengths below 5600 Å excitation of atomic $n\,^2P$ states occurs primarily as a consequence of higher-order effects involving excitation and predissociation into p terms of states resulting originally from d terms. That the necessary potential crossings occur is made probable by the resonant nature of the dispersion forces for p terms giving a long-range R^{-3} dependence and nonresonant forces for d terms with a R^{-6} dependence. As a consequence of the large polarizability for P states, the repulsive energy expected for $p\pi(^3\Pi_g)$ and $p\sigma(^3\Sigma_u)$ terms becomes large even at relatively large internuclear separations, while the d terms could be expected to remain relatively flat.

Excitation of the broadened $n = 8$–10 members of the diffuse series from $6\,^2P_{3/2}$ and the absence of components from $6\,^2P_{1/2}$ at energies below 5600 Å is in agreement with general features expected for the molecular states illustrated in Fig. 1. As discussed in Sec. II, the paucity of states resulting from $6\,^2P_{1/2} + 6\,^2S_{1/2}$, together with selection rules, and the strongly attractive nature expected for $p\sigma(^3\Sigma_g^+)$, make it most unlikely that T_1 resonances can occur for direct excitation to p terms leading to $6\,^2P_{1/2}$ atoms from any of the possible initial populations with wavelengths in the visible region.

Conversely, the $p\pi(^3\Pi_g)$ states with $\Omega = 2, 1$, and 0^- are expected[12] to be strongly repulsive at large internuclear separations and dissociate to $6\,^2P_{3/2}$ atoms offering T_1 resonances corresponding to

$$Cs_2^{**}(^3\Sigma_u^+) + h\nu \rightarrow Cs_2^{**}(p\pi\,^3\Pi_g) \rightarrow Cs^*(6^2P_{3/2}) + Cs\,. \tag{10a}$$

At smaller internuclear separations excitation of the $s\sigma(^1\Sigma_g^+)$ populations could occur through the $^1\Sigma_u^+$ level as illustrated by the arrow marked (2) in Fig. 1,

$$Cs_2^{**}(^1\Sigma_g^+) + h\nu \rightarrow Cs_2^{**}(p\sigma\,^1\Sigma_u^+) \rightarrow Cs^*(6\,^2P_{3/2}) + Cs\,, \tag{10b}$$

or through the $p\pi(^1\Pi_u)$ bound state to energies above the potential barrier to dissociation.[10] For properly resonant photons, either process could lead to T_2 resonances corresponding to $6\,^2P_{3/2} \rightarrow n\,^2D_{3/2,5/2}$ for $n = 8, 9$, or 10. Qualitatively the pronounced broadening of the resulting resonances seen in the $6\,^2P_{3/2} \rightarrow 9\,^2D_{3/2}$ and $6\,^2P_{3/2} \rightarrow 9\,^2D_{5/2}$ components shown in Fig. 5 are in agreement with the substantial kinetic energy which should be possessed by the dissociation fragments of a directly excited $^3\Pi_g$ state. However, the interpretation of the splitting of these lines is more equivocal. That it should occur primarily for directly excited p terms, and not for the d terms giving the fundamental series, suggests the importance of the long-range resonant dispersion forces occurring between P and S atoms. It can be further expected that these splittings are related to the molecular satellites reported[13,21] for absorption lines of the principal series ($6\,^2S \rightarrow n\,^2P$) and in some manner reflect the fact that for these states the T_2 reso-

nance does not occur principally at values of R so large that dispersion forces are negligible. Whether the distinct components seen in Fig. 5 represent transitions from different p terms at large enough R to give splitting of the order of only 1 cm^{-1}, or whether the splitting results from transitions to different d terms at some smaller R cannot yet be resolved. In the latter case the dissociation through some attractive p term would need to be stabilized by either a collision or a substantial centrifugal barrier, and the relative infrequency of the former during the laser pulse would require the initial excitation occur from the more populous lower v of the bound $^1\Sigma_g^+$ state. Should this be the case, the relative number of components split from the $6\,^2P_{3/2} \rightarrow 9\,^2D_{3/2}$ and $6^2P_{3/2} \rightarrow 9\,^2D_{5/2}$ lines is in general agreement with the number of transitions to the different d terms resulting from $D_{3/2}$ and $D_{5/2}$.

Examinations of the intensity dependences in these cases does not tend to distinguish between possibilities, rather indicating considerable complexities resulting from further intensity-dependent shifting and broadening of the split components, presumably by the high fields at the laser focus.

Further clarification of the excitation of the p terms will apparently depend upon independent variation of the wavelengths of the two photons involved, as discussed above. Such a system could be implemented with synchronous dye lasers and would serve to support a more detailed molecular photodissociation spectroscopy with direct identification of the dissociation products. The viability of such a technique is strongly indicated by the results of this work which substantiates the occurrence and importance of multiphoton excitation through potentially resonant continuum molecular states.

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†Work conducted as part of the U.S.-Romania Cooperative Program in Science and Technology between The University of Texas at Dallas and the Institute of Physics of Bucharest. Financial support was provided in part by the U.S. National Science Foundation under Grant No. GF-443 and in part by the Romanian Comitetul de Stat pentru Energia Nucleara and the Consiliul National pentru Stiinta si Technologie.

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