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Citation: *The Journal of Chemical Physics* **93**, 4637 (1990); doi: 10.1063/1.458703

View online: <http://dx.doi.org/10.1063/1.458703>

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# Predissociation of the $\text{Cs}_2$ $C^1\Pi_u$ state

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(Received 29 March 1990; accepted 21 June 1990)

By scanning the frequency of a single-mode dye laser crossed to a molecular beam of  $\text{Cs}_2$ , we measured the excitation spectra of the  $C^1\Pi_u-X^1\Sigma_g^+$  transition by detecting selectively the molecular fluorescence and the emission from the dissociated  $\text{Cs}(6^2P_{3/2})$  atoms. Dependence of the predissociation on each vibrational and rotational level  $C^1\Pi_u(v, J)$  is studied by comparing the intensities of molecular fluorescence and atomic emission. This predissociation is found to depend strongly on the vibrational quantum number  $v$  but weakly on the rotational quantum number  $J$ , and to occur most strongly around the  $v = 3$  level. The Franck-Condon factors between the RKR potential curve of the  $C^1\Pi_u$  state and several repulsive potential curves are calculated, and are compared with the observed predissociation rates. The potential curve of the  $(2)^3\Sigma_u^+$  state, which is expected to be repulsive and to cause the predissociation through the spin-orbit interaction, is estimated to cross the potential curve of the  $C^1\Pi_u$  state between the left turning points of  $v = 1$  and  $v = 0$  levels.

## I. INTRODUCTION

When cesium vapor was excited by the 632.8 nm line of a He-Ne laser, the atomic  $D$  lines as well as the molecular fluorescence of the  $C^1\Pi_u-X^1\Sigma_g^+$  transition were observed. The atomic emission at 852.3 nm ( $6^2P_{3/2}-6^2S_{1/2}; D_2$  line) was much stronger than the atomic emission at 894.6 nm ( $6^2P_{1/2}-6^2S_{1/2}; D_1$  line), and the source of the  $D_2$  atomic emission was identified as the spontaneous predissociation of the  $C^1\Pi_u$  state through a  $^3\Sigma_u^+$  state of repulsive potential.<sup>1</sup> The enhancement of the predissociation by the external magnetic field was also observed.<sup>2</sup> In order to elucidate the predissociation mechanism, it is important to study the vibrational and rotational quantum number dependence of the predissociation. Extensive studies of high resolution spectroscopy for the  $C^1\Pi_u$  state were reported.<sup>3-7</sup> Raab *et al.*<sup>6</sup> studied the  $C^1\Pi_u-X^1\Sigma_g^+$  and the  $D^1\Sigma_u^+-X^1\Sigma_g^+$  bands by using the techniques of Doppler-free polarization spectroscopy and optical-optical double resonance. They observed a broadening of the lines and suggested the predissociation.

In order to study the predissociation more directly, we measured separately the intensities of the  $D_2$  atomic emission and of the  $C^1\Pi_u-X^1\Sigma_g^+$  molecular fluorescence as a function of frequency of a tunable dye laser. We shall call these, respectively, as "excitation spectrum monitored by the  $D_2$  atomic emission" and "excitation spectrum monitored by the molecular fluorescence". This method was shown to be useful for studying the perturbation and predissociation.<sup>8</sup> In order to avoid the effects of dissociation induced by collisions and to obtain a Doppler-free high resolution spectrum, we excited a collimated molecular beam by a single-mode dye laser. Thus, we derived the vibrational and rotational quantum number dependence of the predissociation. We shall report the observed results and discuss the predissociation mechanism.

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## II. EXPERIMENTAL

A block diagram of the experimental setup is shown in Fig. 1. The cesium beam was generated by an oven cell equipped with an orifice of 300  $\mu\text{m}$  diameter in a high vacuum chamber ( $< 10^{-6}$  Torr). We put cesium metal (2 g) in the oven cell, which was heated and kept at 400  $^\circ\text{C}$ . The cesium beam was collimated by a conical skimmer of the inner diameter of 1 mm and crossed at right angles with the laser light. The distance between the nozzle and the skimmer was 5 cm, and the cesium beam was trapped by a liquid-nitrogen trap set. The beam contains mainly Cs atoms, a small amount of  $\text{Cs}_2$  molecule, and a trace of higher clusters. By scanning the frequency of a single-mode dye laser, we measured the excitation spectrum by monitoring the fluores-

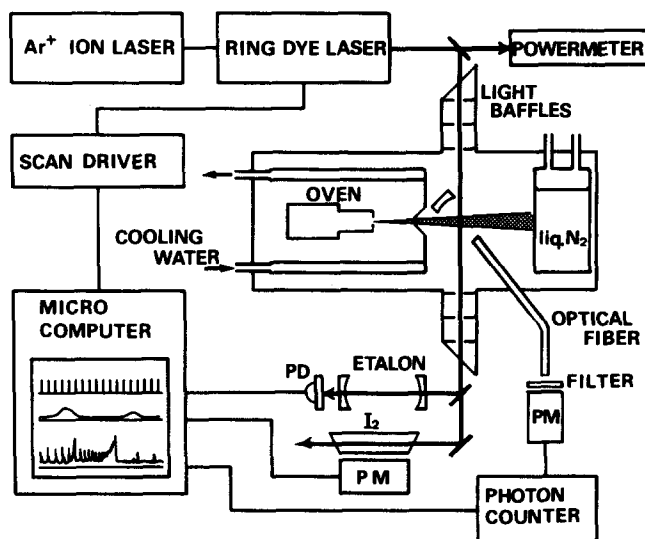


FIG. 1. Schematic diagram of our experimental setup.

cence from either the excited molecules or the dissociated  $\text{Cs}(6^2P)$  atoms. From the rotational and vibrational line spacings of the excitation spectra, we identified the spectral lines as originating from the  $C^1\Pi_u-X^1\Sigma_g^+$  excitation of the  $\text{Cs}_2$  molecule. The contributions from the Cs atom and the higher clusters are negligible for the present study. The emission was collected using a concave mirror and detected by a red-sensitive photomultiplier (Hamamatsu R943-02) and a photon-counting system (Hamamatsu C767). We used the interference filter (band transmittance from 635 to 665 nm) to detect the fluorescence from the  $C^1\Pi_u$  state of the  $\text{Cs}_2$  molecule, and appropriate interference filters to detect selectively the  $D_1$  or  $D_2$  line emission from the dissociated Cs atoms. The relative intensity responses of our optical system at the pass bands of the interference filters were measured by using a standard lamp (Ushio, No. 701038) and the record of an examination for the lamp.

A single-mode ring dye laser (Coherent CR699-29, linewidth 500 kHz) was used as an exciting light source. The absolute wave number of the observed spectral line was calibrated by the fluorescence excitation spectrum of iodine molecule, and the fringe patterns of a confocal etalon (FSR = 150 MHz), which were recorded simultaneously, were used as a frequency marker. The spectral linewidths are mostly 15 MHz in FWHM, and the origin is mainly the residual Doppler width. The absence of saturation effect was confirmed by measuring the linearity of emission intensity and the invariance of linewidth on the laser power. When the laser power was very strong, the saturation broadening of the lines was observed.

### III. RESULTS AND DISCUSSION

The excitation spectrum in the region of 15 919.15–15 919.45  $\text{cm}^{-1}$  monitored by the molecular fluorescence and the one monitored by the  $D_2$  atomic emission are shown in Fig. 2. The observed lines were assigned by using the molecular constants reported in Ref. 6. The lines of the  $C^1\Pi_u(v'=12, J')-X^1\Sigma_g^+(v''=9, J'')$  transition are

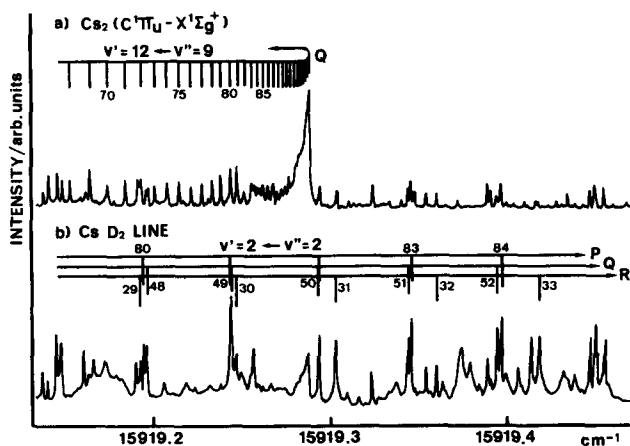


FIG. 2. Excitation spectra of  $\text{Cs}_2$  around 15 919  $\text{cm}^{-1}$ . (a) Excitation spectrum monitored by the molecular fluorescence of the  $C^1\Pi_u-X^1\Sigma_g^+$  transition. (b) Excitation spectrum monitored by the  $D_2$  atomic emission. Assignments of the main series of lines are shown.

prominent in the excitation spectrum monitored by the molecular fluorescence. On the other hand, the lines of the  $C^1\Pi_u(v'=2, J')-X^1\Sigma_g^+(v''=2, J'')$  transition are much stronger than those of the  $C^1\Pi_u(v'=12, J')-X^1\Sigma_g^+(v''=9, J'')$  transition in the excitation spectrum monitored by the  $D_2$  atomic emission. The excitation spectra in the region of 15 934.75–15 935.05  $\text{cm}^{-1}$  are shown in Fig. 3. The lines of the  $C^1\Pi_u(v'=4, J')-X^1\Sigma_g^+(v''=3, J'')$  transition are prominent in both excitation spectra monitored by the molecular fluorescence and by the  $D_2$  atomic emission.

Similar spectra were observed in the region of 15 885–15 956  $\text{cm}^{-1}$ , and about 3500 lines of  $J'=10$ –161 and  $v'=0$ –11 were assigned. Raab *et al.*<sup>6</sup> found small perturbations at  $v'=7, 9$ , and 10. We could not find any other significant energy shifts of the rotational lines. We found that the predissociation depended moderately on  $J'$  but strongly on  $v'$ . When we measured the excitation spectrum monitored by the  $D_1$  atomic emission, we could not observe any spectral lines. Hence, the predissociation of the  $C^1\Pi_u(v', J')$  levels studied in this work is confirmed to occur through the state which decomposes selectively into two atoms in the  $6^2P_{3/2}$  and  $6^2S_{1/2}$  states.

The dependence of the predissociation rate on  $v'$  and  $J'$  is studied by comparing  $I_M(v', J')$  and  $I_A(v', J')$  for a transition to the vibrational and rotational level  $C^1\Pi_u(v', J')$ , where  $I_M(v', J')$  is the intensity of excitation spectrum monitored by the molecular fluorescence and  $I_A(v', J')$  is the intensity of the excitation spectrum monitored by the  $D_2$  atomic emission. The ratios  $I_A(v', J')/I_M(v', J')$  for the P, Q, and R lines are almost the same, and we shall denote the averaged value simply as  $I_A(v', J')/I_M(v', J')$ . The values of  $I_A(v', J')/I_M(v', J')$  were found to depend moderately on  $J'$ . Hence, we averaged the values for  $J'$  from 40 to 60, and adopted this value as the intensity ratio  $I_A(v')/I_M(v')$  which is independent of  $J'$ . This ratio  $I_A(v')/I_M(v')$  is related to  $k_p(v')/k_r(v')$  by

$$I_A(v')/I_M(v') = (B/C_v)k_p(v')/k_r(v'), \quad (1)$$

where  $k_p(v')$  and  $k_r(v')$  are, respectively, the predissociation rate and the radiative decay rate for the  $C^1\Pi_u(v')$  level.

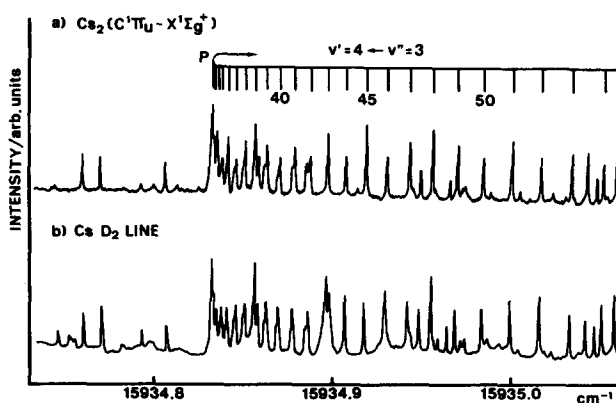


FIG. 3. Excitation spectra of  $\text{Cs}_2$  around 15 935  $\text{cm}^{-1}$ . (a) Excitation spectrum monitored by the molecular fluorescence of the  $C^1\Pi_u-X^1\Sigma_g^+$  transition. (b) Excitation spectrum monitored by the  $D_2$  atomic emission. Assignments of the main series of lines are shown.

$B$  is the ratio of the relative intensity response of our detection system for the  $D_2$  atomic emission to the one for the molecular fluorescence.  $C_v$  is the ratio of the intensity of lines which pass the interference filter to the one of total lines of the  $C^1\Pi_u(v') \rightarrow X^1\Sigma_g^+(v'')$  transitions for all possible  $v''$ . The constant  $B$  was measured to be 0.59. The values of  $C_v$  were evaluated from the Franck–Condon factors and the transition energies for the fluorescence lines from the  $C^1\Pi_u(v')$  level. From these  $B$  and  $C_v$  values and the intensity ratios  $I_A(v')/I_M(v')$ , we have calculated the variation of the ratio  $k_p(v')/k_r(v')$  with  $v'$ , and the results are shown in Fig. 4. It shows that the ratio has the maximum around  $v' = 3$  and decreases gradually as  $v'$  increases.

A possible perturbing state which has a repulsive potential curve and decomposes selectively into two atoms in the  $6^2P_{3/2}$  and  $6^2S_{1/2}$  states is the  $3^3\Sigma_u^+$  state.<sup>1,2</sup> By referring the potential energy curves of  $\text{Na}_2$  and  $\text{K}_2$  molecules, which were obtained by *ab initio* molecular orbital calculations,<sup>9,10</sup> we identified the repulsive state as the  $(2)^3\Sigma_u^+$  state. The perturbation, which causes the predissociation of the  $C^1\Pi_u$  state through the  $(2)^3\Sigma_u^+$  state, is the spin–orbit coupling  $H_{so}$ . The nonvanishing matrix elements between the perturbing states are given by

$$\begin{aligned} \langle ^1\Pi_u f v' J M | H_{so} | ^3\Sigma_u^+ N = J v J M \rangle \\ = (1/2)^{1/2} \xi \langle v' | v \rangle, \\ \langle ^1\Pi_u e v' J M | H_{so} | ^3\Sigma_u^+ N = J + 1 v J M \rangle \\ = [J/2(2J+1)]^{1/2} \xi \langle v' | v \rangle, \\ \langle ^1\Pi_u e v' J M | H_{so} | ^3\Sigma_u^+ N = J - 1 v J M \rangle \\ = [(J+1)/2(2J+1)]^{1/2} \xi \langle v' | v \rangle, \end{aligned} \quad (2)$$

where  $\xi$  is the coupling constant and is assumed to be constant over the internuclear distance of the vibration of  $v'$ .

The present predissociation is observed over a wide range of  $J$  without any important dependence on  $J$ . This type of predissociation occurs through an interaction between a bound state and a dissociative continuum.<sup>11,12</sup> The rate of predissociation is approximately proportional to the product of a Franck–Condon factor  $|\langle v' | v \rangle|^2$  and an electronic–rotational factor  $|\langle C^1\Pi_u J' | H_{so} | (2)^3\Sigma_u^+ N J \rangle|^2$  of the inter-

action. The vibrational wave function  $|v\rangle$  for the dissociative continuum is energy normalized. The Franck–Condon factor is sensitive to the potential energy curves of the mutually perturbing states. The potential curve of the  $C^1\Pi_u$  state is well established.<sup>6</sup> We shall estimate the potential curve of the perturbing state so as the resulting Franck–Condon factors to reproduce the observed variation of the predissociation rate with  $v'$ .

There are three cases of predissociation,  $c^-$ ,  $c^i$ , and  $c^+$ , by Mulliken's classification with respect to the crossing point of the two potentials.<sup>11</sup> By calculating the Franck–Condon factors, Murrell and Taylor<sup>13</sup> studied the predissociation probabilities for the vibrational levels of a bound state of a diatomic molecule crossed by many types of repulsive states. The potential curve of the repulsive state, which leads to the predissociation, is approximated by an analytical function

$$E(R) = X + Y \exp(-\beta R), \quad (3)$$

where  $R$  is the internuclear distance. For appropriate  $X$ ,  $Y$ , and  $\beta$  values, we calculated the Franck–Condon factors for three cases of  $c^-$ ,  $c^i$ , and  $c^+$ , and typical results are shown in Fig. 5. The  $v'$  dependence of the resultant Franck–Condon factors is very different in the three cases. In the case  $c^-$  predissociation, in which a repulsive potential crosses a bound potential at the inner (repulsive) branch, the Franck–Condon factor has a maximum around  $v' = 3$  as shown in Fig. 5(a) and the variation with  $J'$  is moderate. In the case of the  $c^+$  predissociation, in which a repulsive potential crosses a bound potential on the outer (attractive) branch as shown in Fig. 5(c), the Franck–Condon factor varies significantly with  $v'$  and also with  $J'$ . In the case  $c^i$  predissociation in which a repulsive potential crosses with a bound potential at the minimum, the Franck–Condon factor has a maximum at  $v' = 0$  as shown in Fig. 5(b) and the  $v'$  dependence is very sensitive to the slope of the repulsive potential curve. The observed variation of the predissociation rate of the  $C^1\Pi_u$  state with  $v'$  is in good coincidence with the case  $c^-$  as shown in Fig. 5(a). By assuming a repulsive potential of the  $(2)^3\Sigma_u^+$  state as ( $E$  in units of  $\text{cm}^{-1}$  and  $R$  in units of  $\text{\AA}$ )

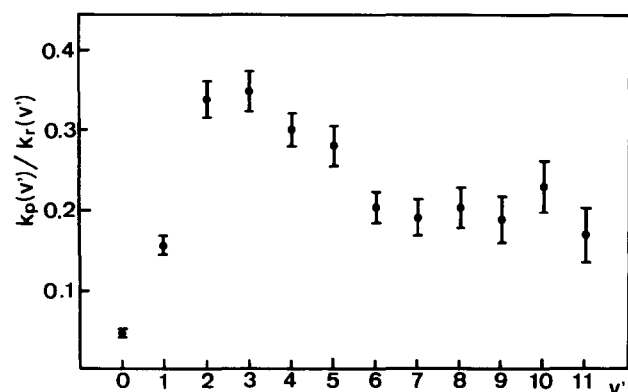


FIG. 4. Variation of the ratio  $k_p(v')/k_r(v')$  with  $v'$ . The fluctuation of the  $k_p(v',J')/k_r(v',J')$  values for the  $C^1\Pi_u(v',J')$  levels of  $J' = 40\text{--}60$  is shown by error bar.

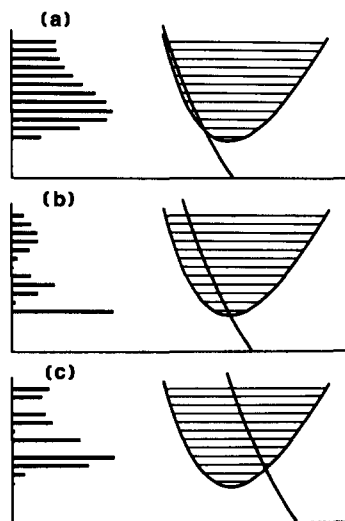


FIG. 5. Three types of crossing between a bound and a purely repulsive state; (a) is the case  $c^-$ , (b) is the case  $c^i$ , (c) is the case  $c^+$ . The bound potential is the RKR potential of the  $C^1\Pi_u$  state. The Franck–Condon factors for these two potentials are shown by the length of the horizontal line. The repulsive potential of (a) is given by Eq (4).

$$E(R) = 15\,381.9 + 3.28 \times 10^5 \exp(-1.45R), \quad (4)$$

which crosses the potential of the  $C^1\Pi_u$  state between  $v' = 1$  and  $v' = 0$ , we could obtain a satisfactory agreement with the observed  $v'$  dependence of the predissociation. Hence, we conclude that the potential curve of the  $(2)^3\Sigma_u^+$  state crosses with the  $C^1\Pi_u$  state between the left turning points of  $v' = 1$  and  $v' = 0$ . We have not found remarkable energy shift nor irregularity of energy spacings in the rotational lines of the  $C^1\Pi_u$  state from  $v' = 0$  to  $v' = 6$ . These observations are consistent with the predissociation through the repulsive potential curve determined above.

We could determine the value of  $k_p(v')/k_r(v')$ , but we could not determine the absolute values of  $k_p(v')$  and  $k_r(v')$ . The linewidths of the spectral lines of the  $C^1\Pi_u - X^1\Sigma_g^+$  transition were about 15 MHz in FWHM. We could not find any line broadening even for the rotational lines of  $v' = 3$ , which are most strongly predissociated between  $v' = 0$  and  $v' = 11$ . This linewidth may be originating from the residual Doppler width, but the linewidth of 15 MHz in FWHM shows that  $k_r + k_p$  is at most  $10^8 \text{ s}^{-1}$ . Hence,  $k_p$  is at most  $3 \times 10^7 \text{ s}^{-1}$  for the level of  $v' = 3$ .

When cesium vapor in an oven cell was excited by the 632.8 nm line of a He-Ne laser, the atomic  $D_2$  line as well as the molecular fluorescence of the  $C^1\Pi_u - X^1\Sigma_g^+$  transition were observed.<sup>1,2</sup> Raab *et al.*<sup>6</sup> found the broad lines in the 632.8 nm region by the Doppler-free polarization spectroscopy and suggested those as originating from the predissociation. The line broadening can occur by other sources, such as the hyperfine interaction. Hence, in order to observe the predissociative lines directly, we measured the Doppler-free excitation spectrum around 632.8 nm by monitoring the  $D_2$  atomic emission, and the results are shown in Fig. 6. The main series of lines are assigned as the rotational lines of the  $C^1\Pi_u(v' = 2) - X^1\Sigma_g^+(v'' = 5)$  and the  $C^1\Pi_u(v' = 6) - X^1\Sigma_g^+(v'' = 8)$  transitions. In addition to these lines, broad lines of FWHM  $\approx 200$  MHz were observed. These broad lines may be assigned as those of the  $D^1\Sigma_u^+ - X^1\Sigma_g^+$  transition. The  $D^1\Sigma_u^+$  state is expected to be more predissociative

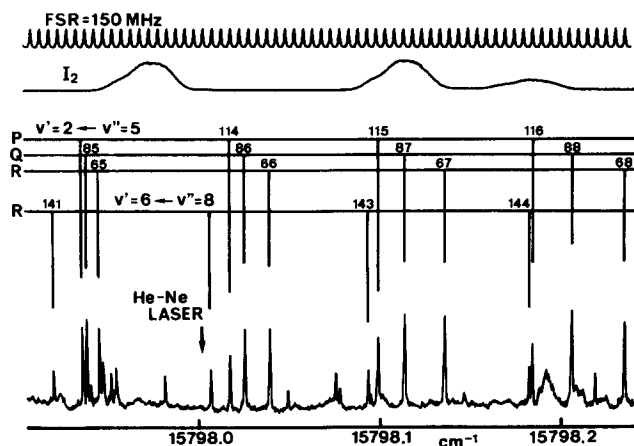


FIG. 6. Excitation spectrum of  $\text{Cs}_2$  around 632.8 nm monitored by the  $D_2$  atomic emission. Assignments of the main lines are shown above. Top line is frequency marks of an external Fabry-Perot interferometer. Second line is the excitation spectrum of  $\text{I}_2$  to calibrate the wave number.

at high  $v'$ ,<sup>6</sup> to which the 632.8 nm line can excite from the high  $v''$  levels of the  $X^1\Sigma_g^+$  state. Actually, in the dispersed fluorescence spectrum of  $\text{Cs}_2$  excited by the He-Ne laser line at 632.8 nm, we observed the fluorescence lines of the  $D^1\Sigma_u^+ - X^1\Sigma_g^+$  transition in addition to the strong lines of the  $C^1\Pi_u - X^1\Sigma_g^+$  transition.

Raab *et al.*<sup>6</sup> suggested the predissociation of the  $C^1\Pi_u$  state to occur at  $v'$  larger than 10. However, our results clearly show that the predissociation of the  $C^1\Pi_u$  state occurs even at  $v' = 0$  and the rate has a maximum at  $v' = 3$ . We carried out similar measurements for higher  $v'$  levels. However, the structure was not clear, so that the assignments were ambiguous and the standard deviations of the least-squares fittings of the molecular constants became remarkably large for  $v' \geq 13$ . These seem to come from the perturbation with another electronic state.

From the  $v'$  dependence of the predissociation rate, we have concluded that the potential curve of the  $(2)^3\Sigma_u^+$  state crosses with the  $C^1\Pi_u$  state between the left turning points of  $v' = 1$  and  $v' = 0$ . The observed linewidths suggest that the predissociation of the  $C^1\Pi_u$  state is weak. On the other hand, the  $D^1\Sigma_u^+$  state seems to be more predissociative at high  $v'$ .<sup>6</sup> From these results, we estimate the adiabatic potential curve of the  $(2)^3\Sigma_u^+$  state as shown schematically in Fig. 7. Around the crossing point with the  $C^1\Pi_u$  state, the  $(2)^3\Sigma_u^+$  state has a character of the  $^3\Sigma_u^+$  state, whose diabatic potential decomposes into  $\text{Cs}(5^2D)$  and  $\text{Cs}(6^2S)$  atoms. A diabatic potential of repulsive curve, which decomposes into  $\text{Cs}(6^2P_{3/2})$  and  $\text{Cs}(6^2S_{1/2})$  atoms, probably extends to the inner potential part of the  $D^1\Sigma_u^+$  state. In order to determine more conclusive curves, more extensive works are necessary on high  $v'$  levels of the  $C^1\Pi_u$  and  $D^1\Sigma_u^+$  states.

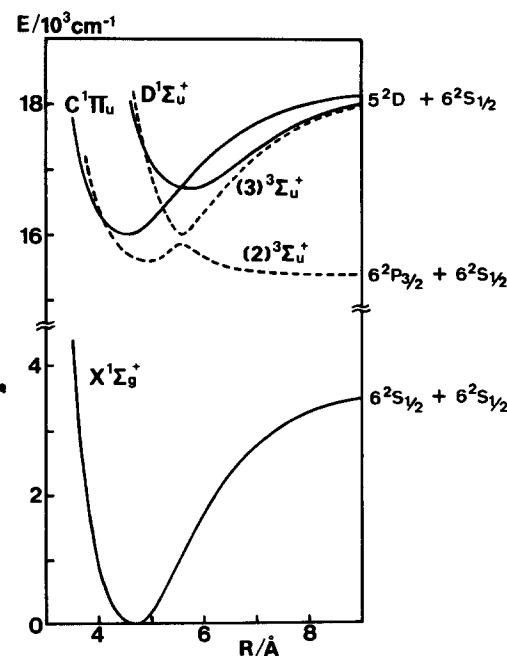


FIG. 7. Potential curves of the  $X^1\Sigma_g^+$ ,  $C^1\Pi_u$ , and  $D^1\Sigma_u^+$  states are the RKR potentials. The broken lines are estimated potential curves, which leads to the predissociation of the  $C^1\Pi_u$  and  $D^1\Sigma_u^+$  states.

## ACKNOWLEDGMENT

M. B. and H. K. thank the Ministry of Education, Science and Culture of Japan for Grant-in-aids for scientific research.

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