Collision-induced dipole transitions and collisional broadening of quadrupole transitions

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Collision-induced dipole transitions and collisional broadening in the wing of Cs(5*D*) due to mixing with Cs(7*S*) and Cs(6*P*) are studied using two-photon resonance ionization spectroscopy. From the structure of the line shape, we measured the van der Waals well of the ground state without performing a temperature study or using the calculated potential curves, and from the absolute yield we measured the induced-dipole oscillator strength as a function of the internuclear separations at large separations. The results are compared with theoretical calculations.

Collision-induced processes have recently received interest theoretically and experimentally.[1–10] The method of resonance ionization spectroscopy[1] provides a very sensitive method for monitoring collisional effects on dipole-allowed and dipole-forbidden processes, and allows considerable reduction of the required absorption tube's temperature and the pressure of the buffer gases.[2,3] The reduction of the pressure reduces such effects as self-broadening, dimer absorption, and three-body processes, thus providing better resolution of the two-body collision parameters.[3]

The study of collisional effects on dipole-forbidden lines has recently received more interest. However, because of the weakness of these lines, the problems encountered in the traditional absorption and fluorescence methods are much more pronounced in this case. The wing of the Cs(6*S*-5*D*) transition was studied by an absorption method using a commerical dual-beam spectrophotometer.[4] The temperature of the absorption cell used ranged from 325 to 405 °C corresponding to 2–20 Torr vapor pressure, and the rare-gas pressure ranged from ~1 to 10 atm. At these densities the absorption due to self-broadening was appreciable; it was necessary to take the absorption spectra with and without the rare gas in order to subtract the effect of self-broadening. The same wing was also studied using a fluorescence method.[5] The method relied on the excitation with a cw light source and the detection of fluorescent light which results from the cascade to the ground state. Optical densities of $10^{15}/\text{cm}^3$ were used to achieve measurable signals; hence making resonance trapping important enough that precise determination of the absolute value of the absorption coefficient was not possible. The oscillator strength of cesium quadrupolar transitions in the absence of foreign perturbers was also studied by an absorption method.[6] Densities in the range 10^{16}–$5\times10^{17}/\text{cm}^3$ were used.

In this paper we study collisional mixing between Cs(5*D*) and Cs(7*S*) wave functions, and mixing of Cs(5*D*) and Cs(6*S*) wave functions with the Cs(6*P*) wave function. The shape of the difference potential of the transition 6*S*-5*D* is sensitive to the first mixing, while the forbidding of the transition is sensitive to the latter mixing.[5] We investigated the mixing by recording the absolute line shape. From the structure of the line shape, we deduced information about the potential curves, and from the absolute yield we measured the induced oscillator strength. The density of the perturber used is 278 Torr so that the many-body effects are eliminated, and hence resolution of the two-body collision may be achieved. Although we use very low optical densities (10^{10} cm^{-3}), we get an excellent signal-to-noise ratio which is far better than the ratio achievable in single-photon absorption measurements.[8] This allows the resolution of fine satellite structure in the wing of the line, which was not observed in absorption measurements; in addition, we have been able to measure the van der Waals well of the ground state without performing a temperature study and without the use of calculated potential curves.

In the present scheme, the excitation is induced by 10-ns pulses and the absorption is monitored by ionizing the excited state; thus directly measuring the absolute absorption by detection of the resulting charge. This scheme avoids the detection of the resonance light, thereby eliminating the problem of resonance trapping. Hence, it allows an accurate determination of the absorption.

The experimental setup is shown in Fig. 1. The output of an Nd-YAG (yttrium aluminum garnet) pulsed laser at 1.064 nm and 10 pps is frequency doubled to 532 nm and used to pump a dye-laser amplifier system. The dye-laser pulses (0.1-Å bandwidth, and 10-ns duration) and few mJ of the main beam at 532 nm are sent collinearly into an ionization chamber which is equipped with plane electrodes and guard plates to isolate the windows and to define the geometry. The chamber is placed in a heated oven with its windows kept at slightly higher temperature than the main body. The Cs sample is introduced in a side nipple under an inert atmo-

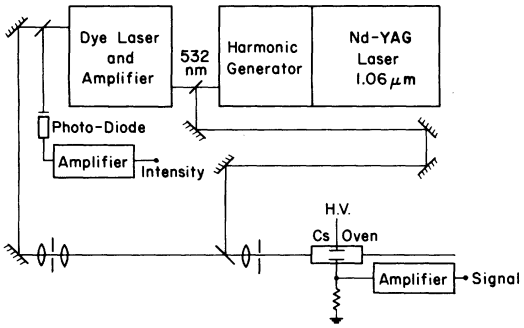

FIG. 1. Block diagram of the experimental setup.

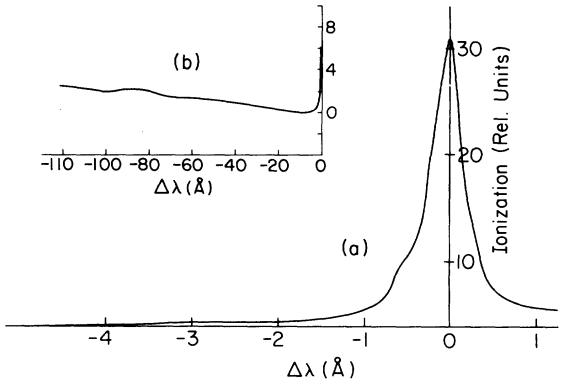

FIG. 2. (a) Line shape of the collisional-broadened Cs(6S)-Cs(5D) quadrupole transition at 278 Torr of Ar buffer gas. (b) The line shape of the collison-induced dipole absorption in the blue wing of the Cs(6S)-Cs(5D) transition at the same Ar pressure. The ordinates of (a) and (b) are the same.

sphere. The collector plate is isolated from ground by a large resistor. The voltage pulse produced across the resistor by the motion of the electrons in the field of the electrodes is picked up by a preamplifier and then amplified. The intensity of the radiation is monitored with a beam splitter and a photodiode, and amplified. Both the ionization signal and the intensity of the radiation for each pulse are stored in a two-dimensional analyzer. The ionization yield can then be displayed as a function of the intensity of the pulses.

A lens of 60-cm focal length focuses the beams to a spot of 0.4-mm diam at the center of the collector plate. At the ends of the plate, 2.5 cm for the middle, the beam focuses to 0.6-mm-diam spot. The electrons produced are collected with 100% efficiency by applying an electric field of 150 V/cm across the plates. The intensity of the photoionizing green beam is chosen such that the ionization step is nearly saturated; so that the ionization reflects the absorption. The ionization yield was studied as a function of the intensity of the ionizing beam. With fixed exciting intensities, the yield at $\Delta\lambda = 0$ as a function of the intenstiy of the ionizing beam is nonlinear with nearly 85% saturation.

Figure 2 shows the absolute line shape of the $6S$-$5D$ transition at 278 Torr of Ar pressure. The main peak of the line shape is the atomic $6S$-$5D$ quadrupole transition. It is asymmetric as a result of a slightly extended blue wing. This blue wing reflects the inelastic collisional broadening of the quadrupole transition. In the rest of the paper we analyze the line shape to test the effect of mixing and compare with theoretical predictions.

Figure 2 shows that for $\Delta\lambda < -5$ Å, the blue wing starts taking off; at $\Delta\lambda = -100$ Å, the wing rises to almost 20% of the main atomic yield. This extending blue wing is due to collision-induced dipole transitions where the collision causes mixing of the wave functions and hence results in an induced dipole moment. The tail shows an enhancement at -88 Å (187 cm^{-1}) in the wing. The resolved satellite indicates the presence of a minimum in the difference potential of the transition at $V = 14\,610$ cm^{-1}. The satellite at $\Delta\lambda = -88$ Å indicates the presence of a well in the difference potential at $V = 14\,790$ cm^{-1}. This satellite will be explained via a well in the potential energy of the ground state Cs(6S)-Ar.

We have been able to measure the well depth of the ground state directly from the line shape of the two-photon ionization. The well depths in potential curves are usually measured by two methods. One method involves scattering between the two atoms in question. It can be accurate; however, it is quite involved. The other method relies on the temperature study of the absorption at the bottom of the well. Plotting the log of the normalized absorption as a function of the inverse of the absolute temperature gives the energy of the ground state. Although this method is less involved than the scattering method, it is less accurate. It was applied to the Cs–noble-gas system with results of $\sim 100\%$ error; the measurement gave 70 ± 50 cm^{-1} for the Cs-Ar system.

Since the well depth of the Cs(6S)-Ar ground state is calculated to be shallow and to extend over a few a.u. distance while the potential of the excited state Cs(5D)-Ar is quite repulsive and structureless, the slope dV/dR^3, where V is the difference potential and R is the internuclear separation, is fairly constant across the well. The variation, however, due to the Boltzmann factor $\exp(-V/kT)$ is more pronounced and expected to dominate the line shape. This enhancement is measured to be 0.22 of the blue tail it is riding on at 300 K. Taking $\exp(-\Delta V/kT) = 1.22$ gives -43 cm^{-1} for the depth of the well. This is in agreement with previous scattering measurements[9] (-45 cm^{-1}) of the ground-state well at 10.4 a.u. and with Pascale and Vandeplanque (PV) calculations -44.4 cm^{-1}.[10] We now calculate the energy of the Cs(5D)-Ar state at 10.5 a.u. from the position of the

satellite. The peak of the satellite at $\Delta\lambda = -88$ Å (187 cm^{-1}), which corresponds to excitation wavelength ~6745 Å, gives 14 826 cm^{-1} for the difference potential at $R = 10.5$ a.u. Using the measured ground-state well depth 43 cm^{-1}, we find that the Cs(5*D*)-Ar potential is 182 cm^{-1} at 10.4 a.u. At this distance, the PV calculation gives 178 cm^{-1}, which shows a remarkable agreement with our measurement. This conclusion is contrary to the widely perceived notion that the PV calculations are expected to be inaccurate.

The satellite at $\Delta\lambda = -0.6$ Å is not characteristic of the ground-state well since it is less than 0.3 Å wide. Nevertheless, excitation from the bottom of the ground-state well to one of the other sublevels of the Cs(5*D*)-Ar state, namely, $m = \frac{5}{2}$, may produce a satellite in the blue wing of the line. At 10.4-a.u. internuclear separation, the energy of the state Cs(5*D*, $m = \frac{5}{2}$)-Ar is 14 558.06 cm^{-1}. Therefore, at this distance, the change in slope may result in a satellite at a 14 602.48-cm^{-1} transition frequency or 5.6 cm^{-1} (2.8 Å) in the blue wing of the line. We believe that the resolved satellite is due to a well in the adiabatic potential of the excited state Cs(5*D*, $m = \frac{1}{2}$)-Ar. The PV calculation predicts an attractive minimum in the adiabatic potential of Cs(5*D*, $m = \frac{1}{2}$)-Ar pair at ~13.9-a.u. internuclear distance. The energy of the ground state at this distance is -20 cm^{-1} relative to the energy at infinite internuclear separation. At this internuclear separation, the satellite then predicts that the adiabatic potential of the excited state of the pair, Cs(5*D*)-Ar, is attractive; its energy is -18 cm^{-1}, where as the PV calculation gives -22.5 cm^{-1} for this energy.

We measured the oscillator strength on the wing of the $6S$-$5D_{5/2}$ ($m = \frac{1}{2}$) transition for several detunings, ranging up to $\Delta\lambda = -100$ Å. The procedure used was as follows. The ionization signal on the wing was compared to the signal at the line center of the quadrupole transtion. Taking the degree of photoionization to be the same for atoms excited at the wing as for those at the line center, σ_{wing} was found in terms of the quadrupole value σ_{quad}. The absorption coefficient was then given by $K(\lambda) = \sigma_{\text{wing}} n_{\text{Cs}}$. Since the other observations we had made of the wing of the $6S$-$5D$ supported the accuracy of the Pascale-Vandeplanque calculations of the potential curves in this region, we made use of these results. The calculated potentials of Cs(6*S*)-Ar and Cs($5D_{5/2}$, $m = \frac{1}{2}$)-Ar allowed us to find $R(\lambda)$, the interatomic separation at the curve crossing, and $dR/d\lambda|_R$, the slope of the difference potential. Substituting the values of λ, $K(\lambda)$, $R(\lambda)$, and $dR(\lambda)/d\lambda$ into the formula

$$f = \frac{Mc}{2\pi\alpha h\lambda^2 R^2}\frac{K(\lambda)}{n_{\text{Cs}}n_{\text{Ar}}}\left[\frac{dR}{d\lambda}\right]^{-1}\exp\left[\frac{V_{6S}(\lambda)}{kT}\right]$$

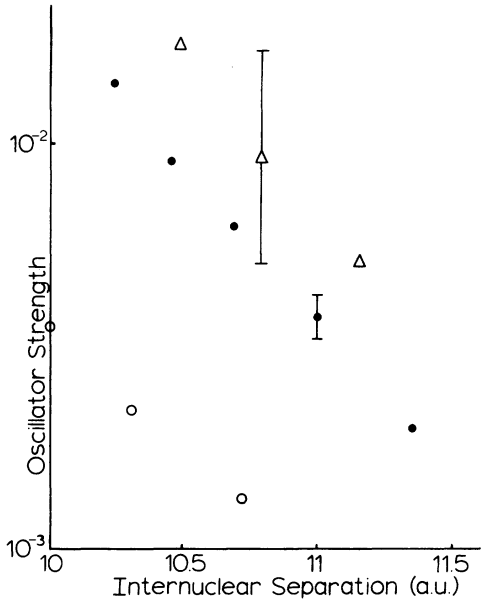

FIG. 3. Measured and the calculated induced dipole oscillator strength in the wing of the Cs(6*S*)-Cs(5*D*) transition. Solid circles are our measurements, open circles are the Pascale-Vanderplanque calculation, and triangles are the Sayer *et al.* measurements.

yielded the results for the dipole-induced oscillator strength at each point on the wing. Our results are shown in Fig. 3 along with the experimental results of Sayer *et al.* and the results of calculations by PV. Our measurements disagree with the PV calculations of the oscillator strengths; however, the disagreement is less than was previously realized. In spite of this disagreement, one can still trust the calculated potential curves, because both calculations are independent of each other. The shapes of the curves depend on the mixing of 5*D* and 7*S*, whereas the induced-dipole oscillator strength depends on the mixing of 5*D* and 6*P*.

The present study indicates that weak transitions can be studied with the resonance ionization method using very low optical densities, thus allowing excellent resolution, and consequently providing very stringent tests for the theoretical predictions. Our measurements indicate the Pascale-Vanderplanque calculations of the potential curves for Cs and Ar are more accurate than is generally recongnized. We have also been able to measure with very good accuracy the well depth of the Cs(6*S*)-Ar ground state, neither performing a temperature study nor using calculated potential curves. In addition, we measured the induced dipole oscillator strength in the wing of the transition with much improved accuracy than was previously achieved in the absorption measurements.

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