Absolute photoionization cross-section measurements of the excited 4*D* and 5*S* states of sodium

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We have measured the absolute cross section for photoionization of the 4*D* and 5*S* excited states of sodium for 1.06 μm radiation. The method of measurement is based on saturation of ionization probability at high intensity of the ionizing radiation. The measured cross sections for ionization of unaligned atoms are 15.2 ± 1.7 Mb for the 4*D* state and 1.49 ± 0.13 Mb for the 5*S* state, both in excellent agreement with calculated values.

I. INTRODUCTION

We have used a saturation method[1] to measure absolute photoionization cross sections of the 4*D* and 5*S* excited states of sodium. Two cw dye lasers are used to stepwise excite a continuous stable population of the 4*D* or 5*S* excited state in an atomic beam, and the number of ions generated by single pulses from a *Q*-switched Nd:YAG laser is measured as a function of ionizing pulse energy. The photoionization cross section is then deduced from the energy at which the photoionization process saturates. This is an attractive method since the only calibration required is that of the ionizing photon flux. The excited-atom density and the absolute number of ions generated need not be known. We have demonstrated that the principal limitation in accuracy can be radiometric calibration and that 10–15% uncertainties are feasible.

Relatively few excited-state atomic[1,2] photoionization cross sections have previously been measured, and for the alkali metals only the first or second *P* states have been studied. Most of the measurements can claim accuracies no better than 30%. Rothe[2] derives photoionization cross sections for Na 3*P* and Li 2*P* from studies of radiative electron-ion recombination in shock-heated plasmas. The more direct measurements of Rb 5*P* and Cs 6*S* by Klyucharev *et al.*[2] and of Li 2*P* by Karlov *et al.*[2] do not use the saturation method, so uncertainties in estimating excited-state populations and ion counts limit accuracy to 30% or greater. More recent results of Ambartzumian *et al.*[1] for Rb 6*P* and Heinzmann *et al.*[1] for Cs 7*P* are based on the saturation method, and the authors quote errors of less than 25 and 10%, respectively. The interpretation of these results is not straightforward, however, because of lack of knowledge about the degree of alignment of the atoms in the excited bound state and polarization of the ionizing radiation, and because of questions about the effects of power saturation of the ground- to excited-state transition. In addition, a proper analysis should take account of spatial and temporal inhomogeneity of the ionizing radiation, spontaneous decay from the excited state, detector linearity, and dynamic Stark shifts. Duong *et al.*[3] have appreciated the importance of atomic alignment and light polarization but have measured only relative cross sections for Na 3*P*. We have overcome many of the difficulties encountered in previous measurements and have obtained the first cross sections for excited *D* and *S* states in an alkali metal. Our results provide a sensitive check on methods of cross-section calculation, particularly for the 5*S*-state calculation which is sensitive to model atomic potentials and where core-polarization effects are significant.[4]

II. METHOD

Figure 1 is a schematic diagram of the experimental apparatus. A well collimated beam of atomic sodium with a density of about 10^9 at./cm^3 is generated in a high-vacuum atomic-beam apparatus.[5] Beams from two stabilized single-mode cw dye lasers are superposed and directed into the Na beam perpendicular to the atomic velocity. The Nd:YAG beam is collinear but incident from the opposite direction for convenience. Positive ions are collected by a weak electric field normal to the laser and atomic beams.

Because cross sections are different for different magnetic sublevels of the bound excited states, a valid cross-section measurement must be made with a well-defined atomic alignment and with well-defined polarization of the ionizing radiation. One simple case occurs when there is equal population of magnetic substates, in which case the average cross section is independent of light polarization. This is a commonly encountered situation but it is not well suited to saturation-based measurements because each sublevel has a different cross section and will saturate at a dif-

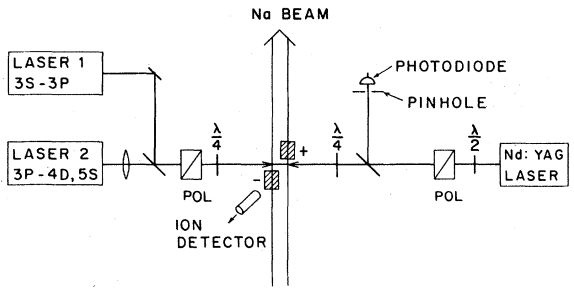

FIG. 1. Diagram of the experimental apparatus.

ferent intensity. Instead, one should ideally populate only one magnetic sublevel and then ionize with light of known polarization.

For the $4D$ cross-section measurement we populate only the $F=4$: $m_F=+4$ level of the $4D_{5/2}$ state. This is accomplished by circularly polarizing the two cw lasers.[6] Laser 1 is tuned to the $3S_{1/2}$: $F=2 \rightarrow 3P_{3/2}$: $F=3$ transition (Fig. 2), so it optically pumps the $3S_{1/2}$: $F=2$ atoms into the $m_F=+2$ level. Thereafter, laser 1 induces transitions to the $3P_{3/2}$: $F=3$: $m_F=+3$ level, and laser 2 populates the $4D_{5/2}$: $F=4$: $m_F=+4$ level. If the Nd:YAG beam is left-circularly polarized (LCP) we produce only F-channel photoelectrons while for the right-circular polarization (RCP) both F and P channels are accessible. This allows an independent measurement for the $D \rightarrow P$ and $D \rightarrow F$ channels. In the L-S coupling the cross sections for the two polarizations are related through angular-momentum algebra to the cross sections applicable to unaligned atoms by[7]

$$\sigma^{\mathrm{LCP}}_{4D\rightarrow F} = \tfrac{15}{7}\,\bar{\sigma}_{4D\rightarrow F}\,,$$
$$\sigma^{\mathrm{RCP}}_{4D\rightarrow F,P} = \tfrac{1}{7}\bar{\sigma}_{4D\rightarrow F} + 3\bar{\sigma}_{4D\rightarrow P}\,. \qquad (1)$$

The σ's to the left of the equality symbol are the values we measure. Those on the right are cross sections averaged over all magnetic sublevels and are the values usually quoted.

Rather than obtaining saturation curves for both circular polarizations of the Nd:YAG laser, we find $\sigma^{\mathrm{LCP}}_{4D\rightarrow F}$ from a saturation curve and then measure the ratio of ion yields for left- and right-

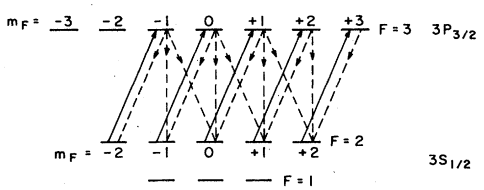

FIG. 2. Diagram of optical pumping process. Solid lines are laser-induced transitions and dashed lines are spontaneous decay transitions. Not shown: $F=0$, 1, 2 levels of the $3P_{3/2}$ state.

circular polarizations with Nd:YAG intensity attenuated so we are not saturating the ionization step. This gives $\sigma^{\mathrm{LCP}}_{4D\rightarrow F}$ and $\sigma^{\mathrm{RCP}}_{4D\rightarrow F,P}/\sigma^{\mathrm{LCP}}_{4D\rightarrow F}$, from which we can deduce $\bar{\sigma}_{4D\rightarrow F}$ and $\bar{\sigma}_{4D\rightarrow P}$.

The cross section for photoionization is the same for all levels of an S state, thus for simplicity we linearly polarize all three lasers in the same direction for the $5S$ measurement. Cross sections are derived by matching experimental saturation curves to saturation curves computed for hypothetical cross sections using a least-squares fitting procedure. Our computed curves take into account spontaneous decay of the excited state, the production rate of excited atoms, and the ionizing pulse shape.

III. EXPERIMENTAL DETAILS

The two cw dye lasers are operated single mode and are frequency stabilized by locking to stable external reference cavities. Their linewidths are approximately 1 MHz and thus are much less than the homogeneous linewidths of the transitions involved. Drift is typically less than 1 MHz over the 60 sec or so required to obtain a saturation curve, and amplitudes are also stable to a few percent over this time. With these lasers the hyperfine structures of the $3S_{1/2}$, $3P_{3/2}$, and $5S_{1/2}$ states are resolved, but the approximately 5-MHz hyperfine structure of the $4D_{5/2}$ state is not resolved. The lasers are tuned to the transitions as shown in Fig. 3 for the two cases. Laser 2 is focused to a 100-μm diameter spot in the sodium beam and is attenuated well below the saturating intensity for the transition it is exciting. This focal spot determines the volume in which $4D$ or $5S$ population is produced. For the atomic beam velocity of approximately 8×10^4 cm/sec, the $5S$ and $4D$ atoms travel less than 70 μm in a natural lifetime. The light from laser 1, unfocused and with a diameter of about 1 cm, is superposed on the beam from laser 2. This larger beam diameter allows ample interaction time for optical pumping before the atoms encounter the focused light from laser 2.

The Q-switched Nd:YAG produces 8 nsec full-width at half-maximum (FWHM) pulses with peak powers of 2–3 MW. Power reaching the interaction region is varied by rotating a half-wave retardation plate in front of a linear polarizer. An intracavity circular aperture 2 mm in diameter defines the transverse intensity profile which is nearly Gaussian in the far field. This beam, with a diameter of a few millimeters, is centered on the focal spot from laser 2 so the ionizing intensity is nearly uniform in the region of excited-state populations. The ionizing intensity is monitored by a photodiode behind a 50-μm pinhole placed in a

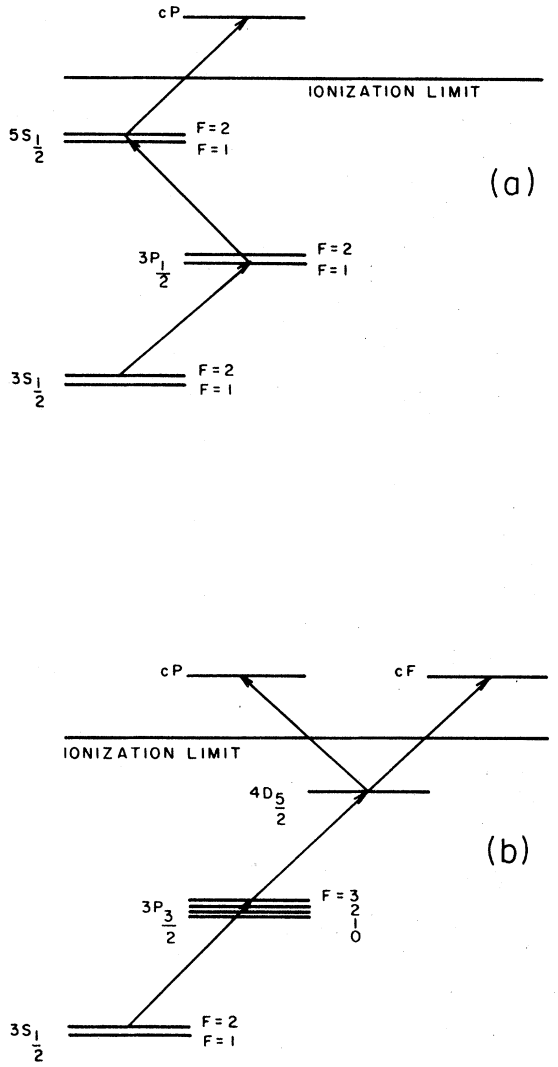

FIG. 3. Diagram of Na energy levels of interest in (a) the 5S measurement and (b) the 4D measurement. Arrows represent laser-induced transitions.

position optically equivalent to the region of excited-state population. The photodiode-pinhole combination is then calibrated against an Eppley thermopile which was recently calibrated against a calorimeter at the National Bureau of Standards to an accuracy of 3% for 1.06 μm radiation. For the pinhole-photodiode calibration the Eppley was placed behind another pinhole of known area also located at a point optically equivalent to the region of excited-state population. Because of the low average power to the thermopile, the accuracy of our intensity calibration is limited to about 7%, primarily due to drift in thermopile output. Scanning a 50-μm pinhole across the Nd:YAG beam reveals variation in intensity of less than 3% over the 100 μm at beam center.

A set of Helmholz coils external to the vacuum system cancels the ambient magnetic field in the interaction region and imposes a field of 1–2 G along the direction of the light beams to prevent mixing among magnetic sublevels. We check the degree of optical pumping by measuring polarization of the fluorescence from the $3P_{3/2}$ state in the forward direction to be sure only the $m_F=+3$ level of the $3P_{3/2}$ state is appreciably populated, and by scanning laser 2 across the $3P_{3/2} \rightarrow 4D$ transitions and comparing ion signals for the $4D_{5/2}$ and $4D_{3/2}$ lines. If pumping were perfect and laser 2 per-

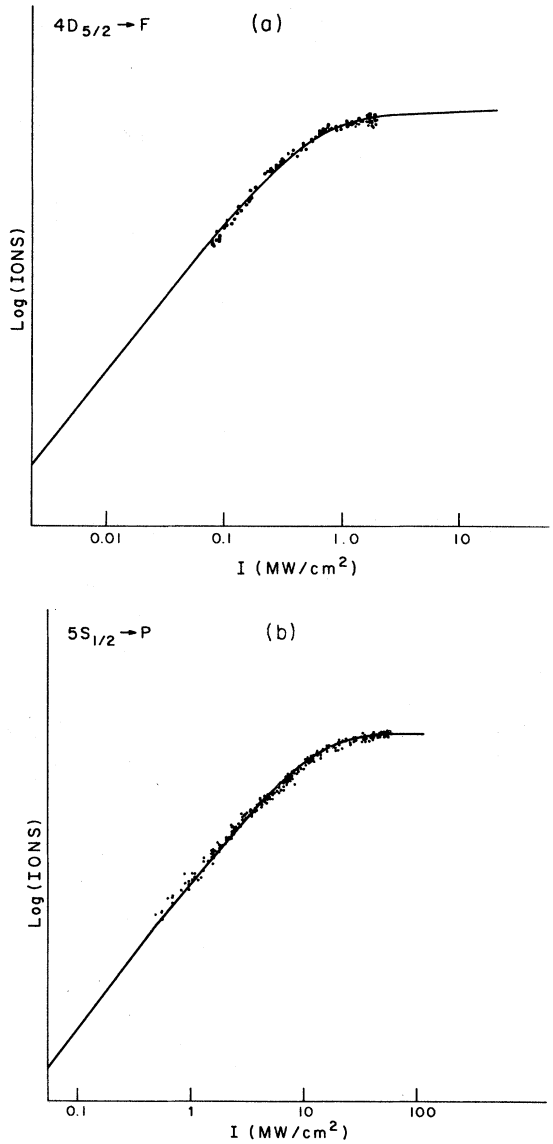

FIG. 4. Dots are data points for single pulses of the Nd:YAG laser. Solid lines are best-fit computed saturation curves.

fectly circularly polarized, the $4D_{3/2}$ line would disappear. From the measured ratio of greater than 400:1 we infer that over 90% of the $3P_{3/2}$ population is in the $m_F=+3$ level and that laser 2 is polarized to greater than 95%. Any population in $4D_{5/2}$ other than in the $F=4$: $m_F=+4$ level is most likely to be in the $F=4$: $m_F=+3$ level. Since this level has a calculated cross section for LCP only 17% smaller than the $m_F=+4$ level and since less than 10% of the $4D$ atoms are in this state, the error in our measured cross section due to incomplete pumping is expected to be less than 2%.

The Na^+ ions are collected by an applied electric field of about 20 V/cm and amplified in an electron multiplier. Our signals are exceptionally free of background because the only populated state which can be ionized by a single 1.06-μm photon is either the $5S$ or the $4D$ state. Background ions produced by multiphonon ionization, associative ionization, or photoionization of sodium dimers and background gas can be observed by tuning laser 2 off resonance. This background is always much less than 1% of the total ion signals.

The ion and monitor photodiode signals are integrated and fed to a minicomputer which plots the logarithm of the ion count versus the logarithm of the integrated ionizing intensity as shown in Fig. 4. Each point represents a single pulse of the Nd:YAG laser.

IV. ANALYSIS

The experimental saturation curves are compared to saturation curves computed by numerical integration of the rate equations over the duration of the ionizing pulse. The rate equations are

$$\frac{dN}{dt}=-N\sigma F(t)+A-\Gamma N,$$
$$\frac{dI}{dt}=N\sigma F(t), \tag{2}$$

where N is the number of atoms in the bound excited state, I is the number of ions, σ is the test cross section, $F(t)$ is the instantaneous flux of 1.06-μm photons, A is a constant production rate, and ΓN is the spontaneous decay rate. Because the ionizing pulse is short (8 nsec) compared to the $5S$ (78 nsec) and $4D$ (50 nsec) natural lifetimes, our results are relatively insensitive to the values used for Γ. Likewise high-frequency fluctuations in $F(t)$ are not very important. The bandwidth of the Nd:YAG laser is irrelevant since the transition is to a structureless region of the continuum. The production rate A is taken to be zero because, at the intensities of interest, dynamic Stark shifts induced by the 1.06-μm light are on the order of 1 GHz. This is a factor of 10 or more greater than the width of the ionization-lifetime-broadened $3P\rightarrow 5S$ or $3P\rightarrow 4D$ transitions, so production of $5S$ and $4D$ atoms is cut off during the ionizing pulse. These shifts have been verified experimentally.[8] The ionizing pulse shape is measured and combined with our energy calibration to find $F(t)$ which is used in the integration procedure. The solid lines in Fig. 4 are best-fit computed saturation curves in which σ is the only free parameter. The uncertainty introduced by curve fitting due to variation of data from run to run and data scatter are about 5%.

TABLE I. Cross sections for unaligned atoms (in Mb).

Measured	Calculated
$\bar{\sigma}_{4D\rightarrow F}=15.2\pm1.7$	14.9
$\bar{\sigma}_{5S\rightarrow P}=1.49\pm0.13$	1.40
$\bar{\sigma}_{4D\rightarrow P}\leq 0.10$	0.007

The cross section values obtained are

$$\sigma^{\mathrm{LCP}}_{4D\rightarrow F}=32.5\pm3.3\ \mathrm{Mb},$$
$$\sigma^{\mathrm{LCP}}_{4D\rightarrow F}/\sigma^{\mathrm{RCP}}_{4D\rightarrow F,D}=14.6\pm1.3, \tag{3}$$
$$\sigma_{5S\rightarrow P}=1.49\pm0.13\ \mathrm{Mb}.$$

Most of the uncertainty arises from difficulties encountered in the radiometric calibrations.

V. CONCLUSIONS

Our cross-section measurements are the first for excited states of the alkali metals other than P states, and we believe our results represent reliable, accurate excited-state photoionization cross sections. We have been careful to specify the atomic alignment when necessary and to otherwise perform the measurement in a manner which leads to straightforward analysis. We believe the quoted error limits are conservative and include all systematic as well as statistical uncertainties. The results for unaligned atoms are summarized in Table I. The calculated cross section $\bar{\sigma}_{5S\rightarrow P}$ is from Aymar.[4] The other two we calculated by the quantum-defect method.[9] The agreement between computed and measured cross sections is apparent in each case.

ACKNOWLEDGMENTS

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[8]By greatly increasing the intensity of laser 2 and scanning it across the atomic transition $3P_{3/2}-4D_{5/2}$ we can, at high ionizing intensity, observe the ions from those atoms which are excited to the $4D_{5/2}$ state during the ionizing pulse. They occur at a frequency of laser 2 shifted relative to the normal resonance produced by those atoms excited before the arrival of the ionizing pulse.

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