Absolute photoionization cross-section measurement of selectively excited magnesium

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We report the first absolute measurement of the cross section for photoionization from a selectively excited short-lived atomic singlet state. Employing two simultaneous tunable laser pulses, the $3s3p\ ^1P_1^o$-$3p^2\ ^1S_0$ autoionization resonance in Mg I was found to have a peak cross section of $(8\pm4)\times10^{-16}$ cm^2 at λ300.9 nm and a half-width of 2.5 nm. The measured ratio of the cross sections to the $3p^2\ ^1S_0$ and $^1D_2$ states was 14:1. The effect of polarization of the lasers has been investigated and shown to provide a means of identifying the angular momentum states of autoionizing levels.

INTRODUCTION

Selective excitation using tunable lasers has allowed the investigation of atomic levels which cannot be reached from the ground state and using these techniques new autoionizing lines have been observed in absorption.[1]

Magnesium, which is of considerable astrophysical interest, has been studied and, in particular, the previously unobserved autoionization transition $3s3p\ ^1P_1^o$-$3p^2\ ^1S_0$ has been located at λ300.9 nm in good agreement with theory.[2] Calculations placed this resonance at λ297.7 nm giving a peak cross section of 12.9×10^{-16} cm^2 in the dipole length and 12.5×10^{-16} cm^2 in the dipole velocity formulation with a resonance width of 137 cm^{-1}.[3]

This paper describes the experimental measurement of the cross section. Measurements of cross sections for photoionization from excited states have been carried out for the laser-pumped ^3D metastable level of barium,[4] for the $6s\ ^2P$ levels of cesium,[5] and for metastable levels of helium excited by electron impact.[6]

EXPERIMENTAL METHOD

As reported previously[2] the $3s3p\ ^1P_1^o$ state of Mg I (lifetime 2 nsec) was populated by a high-power pulse from a laser tuned to the λ285.2-nm resonance line. Attempts to measure the absorption of a second probe laser tuned to the upper-state autoionizing transition were hindered by degradation of the signal-to-noise ratio resulting from scattered light at the excitation wavelength. We have therefore directly recorded the number of photoelectrons produced by a measured laser flux incident on a known number density of excited atoms.

If the density of atoms in the ground and excited states are n_1 and n_2, respectively, then the value of n_2 can be determined from the initial ground-state density n_0 when the resonance transition is saturated. Then we have

$$n_2=\frac{g_2}{g_1+g_2}n_0\ , \tag{1}$$

where $n_0=n_1+n_2$ and g_1, g_2 are the statistical weights of the two levels.

If ionizing radiation at wavelength λ_2 passes through a volume of excited atoms then photoionization proceeds at a rate given by

$$\frac{dN_2}{dt}=-N_2\Phi(\lambda_2)\sigma(\lambda_2)\ , \tag{2}$$

where $\sigma(\lambda_2)$ is the excited-state photoionization cross section, $\Phi(\lambda_2)$ is the ionizing flux density in photons cm^{-2} sec^{-1}, and N_2 is the total number of excited atoms in the interaction volume.

The total number of photoelectrons produced in a time T is then

$$N_e=N_2\{1-\exp[-\Phi(\lambda_2)\sigma(\lambda_2)T]\}\ . \tag{3}$$

Provided the population N_2 is not significantly reduced we may write

$$N_e=N_2\Phi(\lambda_2)\sigma(\lambda_2)T\ ; \tag{4}$$

N_2 is determined by the number density n_2 of excited atoms, the interaction volume defined by the path length L of vapor over which photoelectrons are collected, and the cross-sectional area A of the ionizing beam. Thus

$$N_2=n_2AL\ . \tag{5}$$

When the ionizing radiation is provided by a laser pulse of duration T containing a total number of photons P the average flux is

$$\Phi(\lambda_2)=P/AT\ . \tag{6}$$

Then from Eqs. (4)–(6)

$$\sigma(\lambda_2)=N_e/n_2LP\ . \tag{7}$$

Thus the cross section can be obtained by measuring the total number of photoelectrons produced. Errors arising from measurement of the inter-

action volume are minimized since only the length L needs to be determined.

Equation (7) is valid provided n_2 remains essentially constant throughout the interaction volume and for the duration of the ionizing laser pulse. In the experiment, the upper level is populated by a laser pulse simultaneous with and equal in duration to the ionizing pulse. An estimate of the time taken to saturate the transition to the excited state is given by the time τ_p (the pumping time), and so we must ensure that this is short compared to the laser-pulse duration. This pumping time is given by[7]

$$\tau_p = \left[4\pi^2 \frac{e^2 f_{12}}{mc} \Phi' \right]^{-1}, \tag{8}$$

where f_{12} is the oscillator strength for the resonance transition, Φ' is the photon flux per unit angular frequency interval, e and m are the electron charge and mass, respectively, and c is the velocity of light. This equation was derived on the assumption that τ_p exceeds the dephasing time, which under our experimental conditions was approximately 10^{-11} sec. The duration of the ionizing and exciting laser pulses T was 2×10^{-8} sec and so we arranged τ_p to be approximately 2×10^{-10} sec. This set a lower limit of 8×10^9 photons cm^{-2} sec^{-1} $(rad\,sec^{-1})^{-1}$ for the selectively exciting flux. (This corresponds to a minimum power of 100 $W\,cm^{-2}$ within the Doppler linewidth, or an intensity of 5 $kW\,cm^{-2}$ over the laser bandwidth of 0.04 nm.)

If reduction of n_2 by photoionization was restricted to about 1% then Eq. (4) requires that $\Phi(\lambda)\sigma(\lambda)T \sim 0.01$, thus placing an upper limit on the ionizing flux $\Phi(\lambda_2)$. Since in the case of Mg I, radiation at the resonance wavelength λ_1 can photoionize the excited atoms an upper limit is also placed on $\Phi(\lambda_1)$. Assuming a photoionization cross section at λ285.2 nm of 10^{-17} cm^2, the flux in the exciting laser must be less than approximately 50 $kW\,cm^{-2}$. The intensity within the Doppler-broadened absorption line was therefore restricted to ~1 $kW\,cm^{-2}$, and this limitation determined the total number of atoms which could be saturated over the length of the vapor region.

EXPERIMENTAL APPARATUS

Since the total number of atoms which could be saturated was restricted by the above limitations on the selectively exciting flux the vapor pressure of the magnesium had to be well controlled at low density. A vapor pressure of 2×10^{-5} Torr was established in the central tube of a concentric heat-pipe oven[8] into which helium at a pressure of 100 Torr was added as a dephasing buffer gas. The outer tube operated as a heat pipe with potassium as the working medium, the temperature being controlled by the pressure of the argon buffer gas. This device provided a stable well-defined heated region of magnesium vapor homogeneously mixed with helium whose temperature was kept constant to ±0.1%. The temperature was monitored by a calibrated iron-constantan thermocouple in the inner tube and by measurement of the heat-pipe gas pressure.

The oven, shown schematically in Fig. 1, was fitted with a system of three collinear cylindrical electrodes extending through the vapor region. The central electrode collected electrons over a well-defined length L and the outer cylinders served as guard rings. These outer cylinders were spaced 0.5 mm from the central collector which was formed of a cylinder of titanium foil 50 mm long and 12.5 mm in diameter. The titanium foil, which was resistant to surface corrosion, was perforated to allow a free flow of metal vapor to the central region. A coaxial wire carried a small voltage sufficient to ensure that the device operated on the plateau of the photoelectron current versus voltage curve. The current-voltage characteristic curve, shown in Fig. 2, was determined by generating photoelectrons using two-step photoionization at λ285.2 nm induced by the exciting laser alone. Under saturation conditions the photoionization rate is directly proportional to the power of this pulse. The recorded photoelectron signals could therefore be normalized to the input laser power which was monitored using a fast photodiode and oscilloscope. The capacitance of the system was found to be < 10 pF and so when used with a fast oscilloscope (Tektronix 7904, risetime 0.2 nsec) time resolution of the photoelectron pulse could be achieved.

The dye lasers providing the fluxes $\Phi(\lambda_1)$ and $\Phi(\lambda_2)$ were similar to those described in earlier publications[1] and were simultaneously pumped by the frequency-doubled output of a Q-switched TEM_{00} Nd:glass laser system. Particular care was taken to produce good beam quality in the dye lasers. Not only did this improve the efficiency of the second-harmonic generation necessary to obtain the required uv wavelengths but also avoided spatial saturation effects. Such effects arise when high-intensity filaments or "hot spots" in the beams cause localized depopulation of the $^1P_1^o$ state by photoionization leading to a nonlinear dependence of the photoelectron signal on the ionizing flux intensity.

The first dye laser, used for the selective excitation stage, employed a solution of rhodamine 6G in ethanol as the active medium and was pumped transversely by a fraction of the λ530-nm radiation reflected by a pellicle from the frequen-

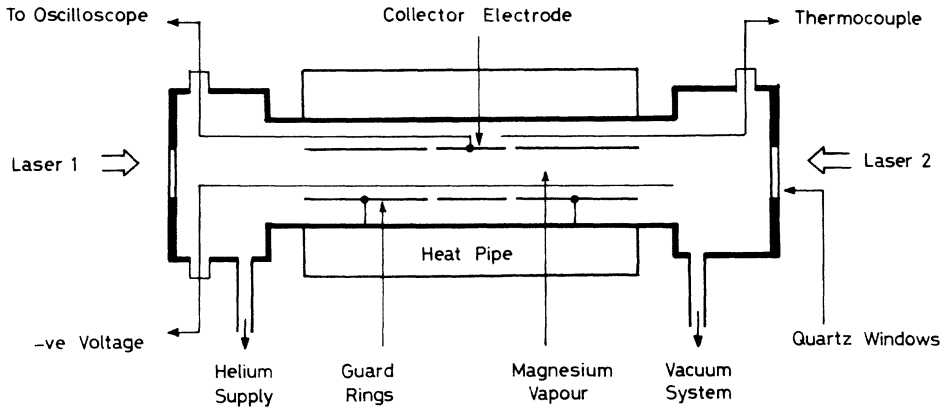

FIG. 1. Heat-pipe oven showing the photoelectron collection system.

cy-doubled Nd:glass laser beam (see Fig. 3). The remaining energy in this pumping beam excited the second dye laser, used to produce the ionizing flux, in which the active medium was an aqueous solution of rhodamine *B*.

The concentration of the dye solutions in both lasers was adjusted to absorb the pumping radiation within a few millimeters. By also adjusting the focused size of the pumping beam the cross-sectional area of the excited active medium could be tailored to produce an effective aperture in the cavity. In this way, low-order or TEM_{00}-mode operation was achieved.

Frequency control of the first dye laser was provided by two intracavity Fabry-Perot etalons and the output, tuned to λ570 nm, had a spectral width of 0.08 nm. When pumped by approximately 200 mJ of λ530-nm radiation an output of typically 50 mJ was obtained which was frequency doubled with up to 25% conversion efficiency. Thus the laser provided 0.5 MW at λ285.2 nm in a pulse of duration 20 nsec with a bandwidth of 0.04 nm. This spectral power density was more than sufficient to saturate the magnesium vapor in the oven.

The second laser contained a single Fabry-Perot etalon and gave an output of spectral width 0.8 nm. The frequency-doubled bandwidth of 0.4 nm was sufficient to resolve the broad autoionization feature of interest. With a pumping energy of about 600 mJ the less efficient rhodamine *B* laser gave an output of typically 100 mJ, which was frequency doubled to give a 0.5-MW pulse at λ301 nm. The second-harmonic frequencies of the dye lasers were generated in ammonium dihydrogen phosphate

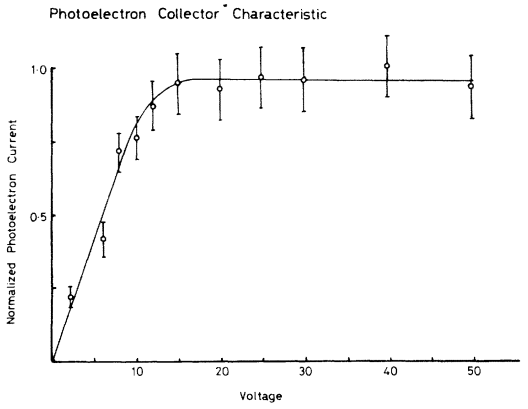

FIG. 2. Electron collecting system characteristic. The photoelectron current signals were obtained using the two-step photoionization process at λ285.2 nm and normalized against the laser power.

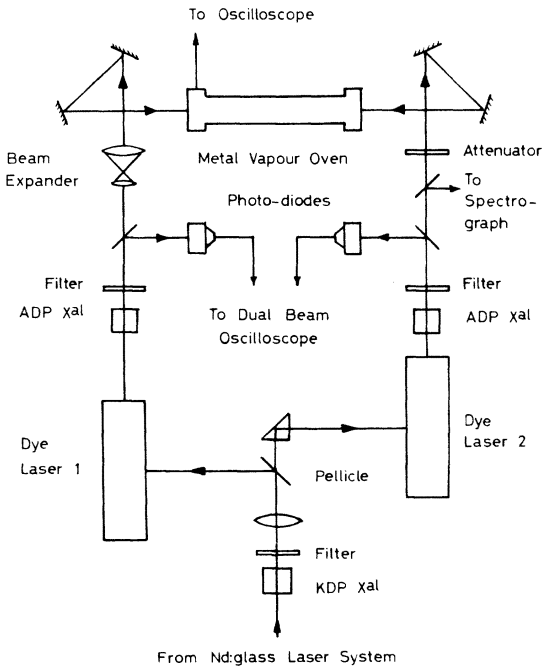

FIG. 3. General experimental arrangement. Laser 1 provided the selectively exciting flux and laser 2 provided the photoionizing flux.

(ADP) crystals angle tuned to achieve phase matching. Detuning these crystals provided a convenient way to adjust the laser power to a suitable level.

EXPERIMENTAL PROCEDURE AND CALIBRATION

The experimental arrangement is shown in Fig. 3. The two laser beams were directed by quartz-prism arrangements to travel collinearly through the electrode system in the metal-vapor oven. The selectively exciting beam was expanded ten times in area to ensure spatial overlap of the ionizing beam with a uniformly pumped region of vapor. Care was taken to ensure that no light was scattered on to metal surfaces inside the oven as this gave rise to spurious signals by photoelectric emission. The cross-sectional areas of the two beams were defined by apertures placed at the entrance windows of the oven.

The intensities of both laser pulses were monitored by fast photodiodes and a dual-beam oscilloscope (Tektronix 556). The photodiode monitoring the ionizing flux $\Phi(\lambda_2)$ was calibrated against an energy meter (Laser Instrumentation 14NO/142LR) at an easily measurable level, typically 10 mJ. The intensity was then attenuated to the desired level using filters calibrated to better than 1% accuracy by a Perkin Elmer spectrophotometer. The wavelength λ_2 was monitored with a 1-m Czerny-Turner spectrograph having a dispersion of 0.8 nm/mm.

The photoelectron detection system had a background noise level of 2 mV which was only 1% of the recorded signals. A typical photoelectron pulse is shown in Fig. 4. As noted earlier the selectively exciting beam at λ285.2 nm could photoionize atoms already in the $3s3p\ ^1P_1^o$ state and with the high powers available it was possible to ionize a significant fraction of the atoms in the path of the beam by this two-step process. Apart from ensuring that this process did not depopulate the excited state, it was necessary to arrange that the resulting signal did not introduce a significantly fluctuating background to the signal produced by the second laser pulse at λ300.9 nm. The signal due to the λ285.2-nm light was kept to about 10% of the overall signal and so variations of 10% in the intensity of this pulse would contribute only 1% error to the measured signal. By monitoring this laser pulse variations could be detected and the background signal could thus be normalized to a given intensity. The recorded signals were very reproducible when normalized to the incident laser powers.

Multiphoton effects, which could also have introduced errors, were investigated. In the absence of the λ285.2-nm laser pulse the λ300.9-nm beam gave no detectable two-photon ionization. A more probable source of two-photon absorption would arise from the range of frequencies of the exciting beam outside the $3s^2\ ^1S_0$-$3s3p\ ^1P_1^o$ absorption line. At sufficiently high-power densities these wavelengths could combine with those of the second laser because of near-resonant interactions. However, when the exciting beam was tuned off resonance by the appropriate amount the recorded signal fell to an insignificant level. Two-photon effects then did not provide an important source of error at the power densities used in this experiment.

As explained before, the power densities were restricted to prevent saturation of the photoionization process. The number densities of atoms used and the degree of ionization produced were also limited to avoid space-charge effects. When the power of the ionizing laser was varied over three orders of magnitude no such effects were observed.

POLARIZATION EFFECTS

The calculations of Thompson, Hibbert, and Chandra[3] treated photoionization of unpolarized magnesium atoms in the $3s3p\ ^1P_1^o$ state by both polarized and unpolarized light. In the present experiment the magnesium is excited by a linearly polarized laser beam and so if no depolarizing effects occur pumping from the $^1S_0$ ($m_J = 0$) ground

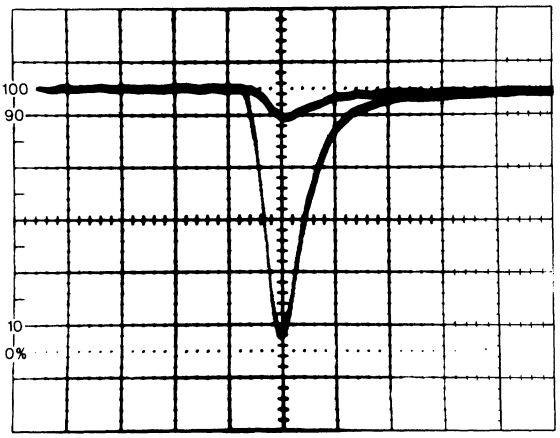

FIG. 4. Typical photoelectron current pulses. The smaller pulse was produced by two-step photoionization at λ285.2 nm. The larger pulse was produced when both laser beams were incident on the Mg vapor. Vertical scale 50 mV per major division; horizontal scale 20 nsec per major division.

state via transitions governed by the selection rule $\Delta m_J = 0$ leads to an array of polarized atoms. Since the photoionizing beam is also linearly polarized it is necessary to ensure that the atoms are depolarized, i.e., the magnetic sublevels are equally populated, during the interaction with the photoionizing pulse. This was confirmed by the following procedure.

If the polarization plane of the exciting laser remains fixed (effectively defining an axis in space) in the absence of depolarizing effects only the $m_J = 0$ sublevel is populated. When the photoionizing laser tuned to the peak of the $3s3p\ ^1P_1^o$-$3p^2\ ^1S_0$ transition is polarized in a plane parallel to this axis then the selection rule $\Delta m_J = 0$ allows a transition to the $^1S_0$ level and a strong photoelectron signal is expected. For orthogonally polarized light transitions to the $^1S_0$ level are forbidden leaving only the weaker transitions to $^1D_2$ states resulting in a smaller signal. If the atoms are rapidly depolarized by collisions or scattered resonance fluorescence then no difference should be observed in the signals.

To detect these effects the oven was evacuated to a pressure of 5×10^{-5} Torr, the absolute pressure being measured with a McLeod gauge, and heated to give a magnesium vapor pressure of 2×10^{-5} Torr. A double Fresnel rhomb was placed in the ionizing laser beam; by rotating this device the beam's plane of polarization could be rotated by $\frac{1}{2}\pi$ without causing any deviation or displacement. Initially the polarization planes of both exciting and ionizing lasers were arranged to be parallel and the photoionization signal was recorded. When the polarizations were made orthogonal the observed signal decreased by a factor of approximately 5. This factor is smaller than expected from the ratio of the $(^1P$-$^1S)$:$(^1P$-$^1D)$ cross sections given by theory as 13:1 and by experiment as 14:1 (see below). Depolarization by background-gas collisions, resonance fluorescence, and incomplete polarization of the light would all contribute to a decrease of the observed ratio. When helium gas was admitted to the oven the difference between the "parallel" and "orthogonal" signals was reduced and disappeared altogether at pressures of about 1 Torr. This indicates that the atoms were completely depolarized by collisions at these pressures; the photoionization cross-section measurements were made with helium pressures well in excess of this value. At higher vapor pressures of magnesium (~10^{-3} Torr) no difference in signals was observed owing to the depolarizing influence of longer-range resonance interactions. It can be seen that under suitable conditions this technique can be used to identify the angular momentum state of autoionizing resonances.

RESULTS

Having measured N_e, P, and determined n_2 from the value of n_0 given by the vapor pressure[9] the absolute photoionization cross section at λ300.9 nm was calculated using Eq. (7). By tuning the ionizing laser the relative cross section was found over the spectral region centered on the $3s3p\ ^1P_1^o$-$3p^2\ ^1S_0$ autoionizing transition. In this way a range of 1200 cm^{-1} was covered and the line shape determined as shown in Fig. 5. Calibration errors and errors in the measurement of the photoelectron current amounted to ±20%. The largest single error was associated with the calculation of the number density n_0; limitations of the vapor-pressure data and inaccuracies of temperature measurement gave an uncertainty of ±30%. Thus we arrived at a value of

$$\sigma(300.9\text{ nm}) = 8 \pm 4\times10^{-16}\text{ cm}^2.$$

The relative cross section was measured with an error of ±15%. Figure 5 shows the experimental data fitted to a computer-drawn Lorentzian curve centered on λ300.9 nm with a full width at half-maximum (FWHM) of 2.5 nm (300 cm^{-1}). These results are in excellent agreement with the calculations of Thompson, Hibbert and Chandra.[3]

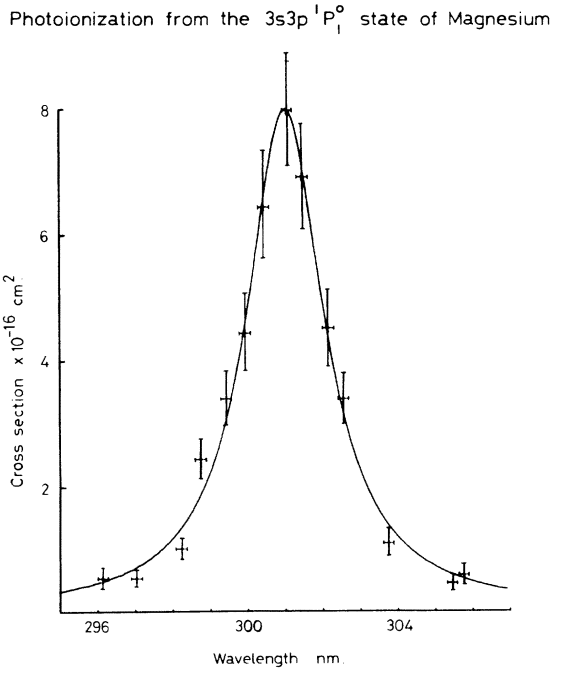

FIG. 5. Relative photoionization cross section obtained by tuning the second laser. The curve is a computer-drawn Lorentzian fitted to the experimental points.

CONCLUSION

The absolute photoionization cross section of a short-lived atomic state has been measured. Increased accuracy in the measurement would result from improved vapor-pressure data. The experimental technique also allows relative cross sections to be determined for astrophysical models and for evaluating isotope-separation processes. Similarly the physical processes occurring in four-wave parametric mixing schemes which involve autoionizing states[10] can be directly studied. These experiments are now under way in our laboratory. It is obviously possible to locate and measure new autoionizing states by this method of selective excitation. Together with the advantage of starting from a well-defined atomic state, variation of the state of polarization of the laser beams aids in identification of the autoionizing states. Alternatively, by appropriate choice of polarization a particular angular momentum state in the continuum can be selected. In this way the relative contributions of different states to the total photoionization cross section could be measured.

A measure of the broadband ^1P-^1D autoionization cross section can be obtained from the background level in Fig. 5. This gives a ratio of 14:1 for the cross section to the ^1S and ^1D states, respectively, again in very good agreement with the results of Ref. 3.

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