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Photoionization of the excited 3p state of sodium: Experiment and theory

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Measurements of the cross section for photoionization of the excited 3p state of sodium have been made over a significant energy range. Calculations at the central-field and Hartree-Fock levels have also been carried out. Agreement between theory and experiment is excellent.

I. INTRODUCTION

The study of excited states of atoms offers an opportunity to investigate relatively simple systems of large physical extent. In addition, ionization processes involve the continuum wave functions of the final states at distances far from the nucleus; this region is inaccessible from ground states owing to their small spatial extent, $\sim a_0$. This is of importance since continuum wave functions are generally the least understood element of ionization theory.

Photoionization is the simplest ionization process since the incident particle disappears upon interaction. Furthermore, excited-state photoionization is of importance in certain hot regions such as stellar atmospheres and CTR (controlled thermonuclear research) plasmas, and is also useful in understanding radiative recombination, the inverse process.

Various theoretical predictions of new phenomenology in excited-state photoionization have been reported.[1–3] These have not yet been tested experimentally. In fact, there is very little experimental work on excited-state photoionization cross sections, and even less which covers a significant energy range. This latter is of great importance for assessing the accuracy of the theoretical work; cross sections at a single-photon energy, while useful, are simply not sufficient for testing theory.

To remedy this we have initiated a joint experimental and theoretical study of photoionization of excited states. In this paper, we report on the photoionization of the excited 3p state of sodium. The experiment uses the unique monochromatic high-intensity capabilities of the laser to populate the initial state, along with the broadband tunability of synchrotron radiation for the ionization process. The calculation was performed using both simple Hartree-Slater and more sophisticated Hartree-Fock wave functions for both initial excited discrete states and final continuum states employing methods described elsewhere.[4–6]

II. EXPERIMENTAL METHODOLOGY

Experiments were performed at both the Brookhaven National Laboratory (BNL) and University of Missouri–St. Louis (UMSL). At BNL we used the facilities of the Department of Chemistry windowed beam line (U9A) at the ultraviolet ring of the National Synchrotron Light Source to determine the relative photoionization cross section of Na(3p) from threshold, 4083 to about 2500 Å. Synchrotron light was dispersed with a 0.5-m Seya-Namioka normal-incidence grating monochromator and the resulting monochromatic beam steered to intersect perpendicularly an effusive beam of sodium atoms whose concentration was $\sim 10^{10}$ cm^{-3}. The beam from a multimode cw dye laser also intersected the sodium-atom beam interpenetrating the synchrotron light. Ions formed at the intersection were electrostatically focused into a quadrupole mass filter and detected with a CuBe multiplier using conventional single-particle counting techniques. The ion signal was measured as a function of the wavelength of synchrotron light with the mass filter setting fixed at 23 amu, and the laser tuned to either the D_1 or D_2 wavelength. Typical dwell times were 2 sec per wavelength setting; the high repetition rate (17 MHz, single bunch mode) of the synchrotron-light pulses permitted the experiment to be carried out in a quasi-cw mode. The data were corrected for variation of (synchrotron) photon flux as a function of wavelength using a sodium-salicylate-coated photomultiplier tube to measure the spectral power of the synchrotron light. The intensity and wavelength of the laser light was monitored by splitting the beam and observing the D-line flourescence with an external sodium cell.

The absolute photoionization cross section at threshold was measured in the Atomic Physics Laboratory at UMSL. Sodium vapor at $\sim 10^{10}$ cm^{-3} was introduced into a rectangular reaction cell from an oven beneath the cell; the Na(3s) density was determined by a method developed in this laboratory.[7] Two antiparallel, interpenetrating pulsed-laser beams, one yellow and tuned to a D-line wavelength and the other blue and tuned to the Na(3p) photoionization threshold, illuminated the sodium vapor. These lasers had pulse lengths of $\sim$ 7 nsec with a repetition rate of 10 Hz and were pumped by the frequency-doubled and -tripled outputs of the same Nd:YAG (where YAG denotes yttrium aluminum garnet) laser. The yellow laser was operated at

~ 1kW per pulse, just sufficient to saturate the $3s \rightarrow 3p$ transition.

One side of the cell was stainless-steel mesh to which a voltage was applied to extract photoions from the cell. After passing through the mesh the ions were detected with a calibrated single-stage microchannel plate. This arrangement permitted collection of all ions formed in the cell and, together with the measurement of the ground-state atom density and knowledge that the $3s \rightarrow 3p$ transition was saturated, led to the determination that the photoionization cross section for Na($3p$) at threshold is 8.5 Mb. The major uncertainty in this determination is that associated with the effective-interaction path length. From geometrical considerations and the measured dependence of the ion signal on the extraction voltage, we estimate this uncertainty to be ~ 25%.

III. RESULTS AND DISCUSSION

The photoionization cross section of Na($3p$) was measured from threshold to ~ 2 eV above threshold. This energy range is about a factor of 4 larger than the range in a previous experiment which employed two lasers.[8] The experimental cross section is shown in Fig. 1, where it is seen that it drops monotonically from threshold, ~ 3 eV. The rise at the high-energy (short-wavelength) end of the curve, near 5 eV, is due to photoionization of the $3s$ electron of ground-state Na atoms and should be ignored for our purposes. This measurement agrees quite well with the results of Ref. 8, and is also entirely consistent with an earlier shock-tube measurement.[9]

Also shown in Fig. 1 are the theoretical cross sections. Excellent agreement with experiment is seen for both of the calculated results as well as between the theoretical cross sections. This shows that the theoretical cross sections are reasonably accurate and implies that theoretical results may be reliable in other cases as well. Furthermore, the agreement between the central-field Hartree-Slater (HS) cross section and the Hartree-Fock (HF) cross section shows that exchange is not of crucial importance so that HS theory will also be useful in other cases. The HF cross section was actually calculated in both dipole-length and dipole-velocity formulations.[4-6] The difference between them is often a measure of the accuracy of the calculation. In this case, they were so close (within 0.5%) that both could not be plotted separately; this gives us further confidence in the theoretical result. In addition, the theoretical results are in quite good agreement with the predictions of two model-potential calculations.[10,11]

Generally, theoretical cross sections are least accurate in the vicinity of a zero in one of the dipole matrix elements, particularly in the dominant $l \rightarrow l+1$ transition. Such a zero exists in the $3p \rightarrow \epsilon d$ transition, but at an energy well outside the range investigated experimentally, at ~ 10 eV above threshold. The cross section is shown in Fig. 2, over a much larger energy region. The zero in the $p \rightarrow d$ dipole matrix element, generally known as a Cooper minimum,[12] shows up as a slight minimum in the HS cross section, but manifests itself only as a dramatic change of slope in the HF cross section. Thus, it is seen from Fig. 2, that the agreement is poorest in the minimum region and much better both above and below the minimum. This, then, allows us to infer that HS results will be relatively good away from Cooper minima, but somewhat suspect in the Cooper-minimum region.

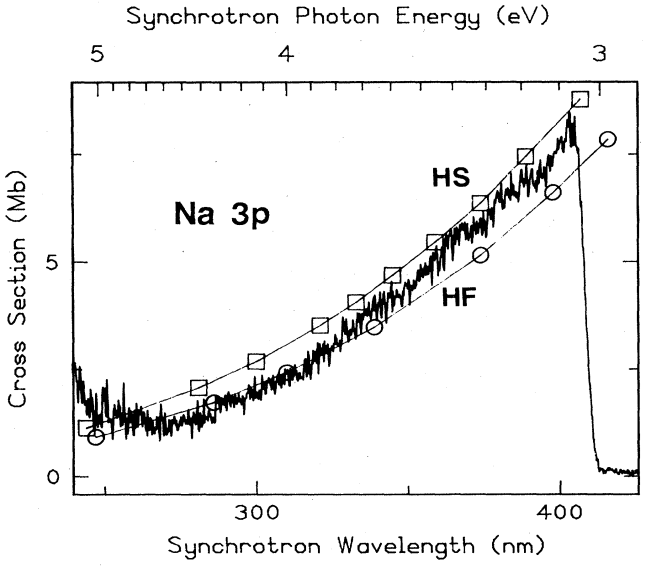

FIG. 1. Photoionization cross section for the excited $3p$ state of Na. Theoretical results are Hartree-Fock (HF) and Hartree-Slater (HS) cross sections. The experimental cross section is absolute and *not* normalized to theory. The experimental data were acquired with a spectral resolution of 40-Å full width at half maximum.

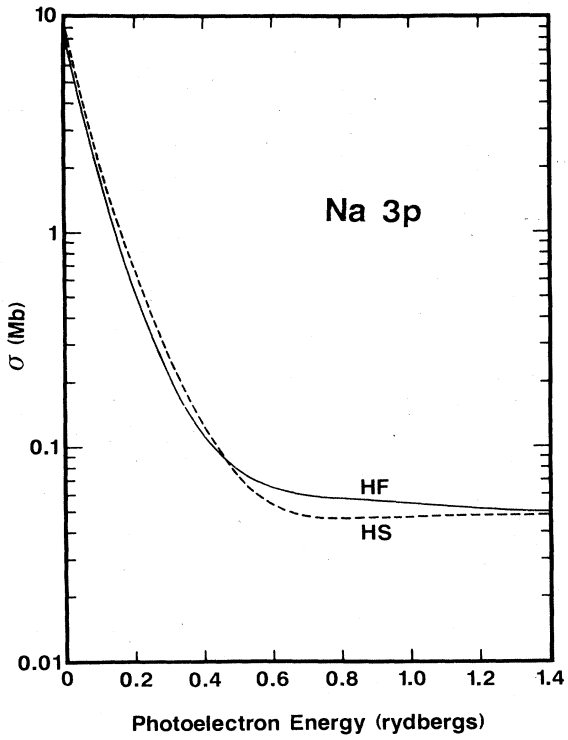

FIG. 2. Theortical photoionization cross section of the excited $3p$ state of Na in Hartree-Fock (HF) and Hartree-Slater (HS) approximations.

IV. FINAL REMARKS

A theoretical-to-experimental comparison of the photoionization cross section of the excited $3p$ state of Na has been made which shows excellent agreement. This comparison has been made over an energy range of $\sim\frac{2}{3}$ of the $3p$ binding energy, the largest range ever measured for an excited state. This benchmark measurement shows the utility of experiments which combine the capabilities of laser and synchrotron radiation. Future plans include extending the energy range and investigating other systems, in an effort to provide a general understanding of excited-state photoionization.

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