Absolute Cross Sections for the Photoionization of the $6s6p\ ^1P$ Excited State of Barium

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Absolute photoionization cross sections for the $6s6p\ ^1P$ excited state of Ba have been measured in the threshold region and found to agree substantially with theory, thus resolving previous discrepancies. Use was made of the "magic" angle applied to the relative orientation of the linear polarizations of the exciting and ionizing lasers; at this orientation angle the measured cross section is the same as if the excited state were populated isotropically. This phenomenon, which has general application to electric dipole photoabsorption processes, allowed us to make the measurements in two different ways, with excellent agreement between them.

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Photoionization of excited atoms is a subject that is of both fundamental and practical importance. From a fundamental standpoint it is a very simple process, an interaction between electromagnetic radiation and a physically large system possessing internal energy. It may therefore may be envisioned as the next step in complexity beyond photoionization of ground-state atoms. From a practical standpoint, the behavior of any assemblage of atoms hot enough to produce excited states in quantity, such as astrophysical or plasma environments, is largely dependent on these processes [1]. Furthermore, excited-state photoionization is the inverse process to low-energy radiative recombination, which is under current scrutiny [2].

Over the past few years a number of studies of excited-state photoionization, both theoretical and experimental, have been performed [3–5]. These studies have concentrated primarily, but not exclusively, on alkali atoms, "one-electron" atoms, for which the only structure in the photoionization cross section near threshold results from interferences between bound and continuum wave functions, e.g., Cooper minima [6]. Examination of alkaline earth atoms, "two-electron" atoms, on the other hand, can lead to rich structure in the near threshold region due to the existence of discrete states embedded in the ionization continuum. The theoretical techniques required to treat this problem are, however, more challenging than for one-electron atoms because proper account of two-electron excitations is crucial. This has been studied extensively for ground-state alkaline earth atoms [7], but it is only recently that theoretical treatments of photoionization of excited alkaline earth atoms have been undertaken. This problem not only provides an extra dimension to that of ground-state photoionization, but it also requires inclusion of states that are generally not accessible from the ground state. It is therefore important that the theory be stringently tested.

Although recent theoretical studies of photoionization of the excited $6s6p\ ^1P$ state of barium have produced results which are in substantial agreement with each other [8–11], they are at variance with some recent experiments [12]. The discrepancies between theory and experiment occur in both the magnitude of the cross section and the location and shapes of the autoionizing resonances caused by the interaction of discrete and continuum states. In an effort to resolve these discrepancies we have undertaken atomic-beam experiments designed to yield the magnitude of the cross section, its energy dependence in the critical near-threshold region, and the locations and shapes of the autoionizing resonances. Further, our experiments have included polarization studies designed to make comparison with theory more rigorous and detailed. Our results are in general agreement with the theoretical work, in both magnitude and structure. They are also in essential agreement with a recent measurement of the *relative* cross section [13].

Our experiments were performed in an atomic-beam apparatus using two laser beams, a green one to excite the $6s6p\ ^1P$ state of barium, 553.7 nm, and a blue one to photoionize this state. The effusive atomic beam was produced by a resistively heated oven located approximately 5 cm below a stainless-steel cell in which the excitation and photoionization took place. The atomic-beam density was always lower than 10^8 cm^{-3} in order to avoid collisional or collective effects. The laser beams were counterpropagating and perpendicular to the atomic beam. Data were acquired with the laser powers sufficiently low so that two-photon, resonance-enhanced, ionizations from photons of a single wavelength, blue, did not appear in the photoionization spectra. Higher laser powers were, however, employed, as described below, for determination of the absolute value of the cross section. We also used relatively high laser powers to cause a pair of known two-photon resonances, both blue, to appear in order to fix the wavelength scale. These resonances are $6s^2\ ^1S_0 \rightarrow 6p'\ ^3D^e_1$ at 413.359 nm and $6s^2\ ^1S_0 \rightarrow 6p'\ ^3P^e_1$ at

389.042 nm, where the prime indicates that the bound Ba state has nominal $5d6p$ configuration. We also checked the wavelengths of each of the observed autoionizing resonances using a calibrated monochromator (± 0.05 nm).

After formation, ions were electrostatically extracted with a very small field, ~ 3 V/cm, and steered to the cathode of a CuBe particle detector, the output of which was fed to a gated charge-sensitive amplifier. The experimentally determined cross sections are thus plots of ion signal (corrected for laser intensity) versus wavelength of the (blue) ionizing laser beam, the bandwidth of which was less than 1 cm^{-1}. Both laser beams were linearly polarized, but the angle between their planes of polarization was set using two Glan-Thompson polarizers, a procedure that allowed direct comparison with theory, as described below.

The initial $6s6p\ ^1P$ state is not pure, but has significant mixing with the $^3P_1$ state owing to relativistic interactions; J is, however, a good quantum number. Thus, for an isotropic (equal population of M_J) initial state, the photoionization cross section, $\sigma^{\rm iso}$, is given by the sum of the cross sections to each of the allowed $J=0,1,2$ final states, $\sigma_J^{\rm iso}$, as

$$\sigma^{\rm iso}=\sigma_0^{\rm iso}+\sigma_1^{\rm iso}+\sigma_2^{\rm iso}. \tag{1}$$

The use of lasers to populate and photoionize the excited state, however, changes matters because their polarization determines the M_J levels which may be populated in a given transition. In our experiment, the linear polarization of the green (553.7 nm) laser beam defines the z direction and assures that $\Delta M_J=0$ so that only $M_J=0$ substates of the $6s6p\ ^1P$ initial state of the photoionization process will be populated. It will therefore *not* be isotropic as illustrated in the energy-level diagram in Fig. 1 which shows the excitation to $M_J=0$ of the $6s6p\ ^1P$ state. Also shown are the possible J and M_J final states. In addition to the restriction imposed by the polarization of the exciting laser beam, the photoionizing laser beam is also linearly polarized so that the measured cross section depends upon the angle θ between the two laser polarization directions, as given by

$$\sigma(\theta)=3\cos^2\theta\sigma_0^{\rm iso}+\tfrac{3}{2}\sin^2\theta\sigma_1^{\rm iso}+\tfrac{3}{10}(3+\cos^2\theta)\sigma_2^{\rm iso} \tag{2}$$

and

$$\sigma(\theta)=\cos^2\theta\sigma^{\parallel}+\sin^2\theta\sigma^{\perp}, \tag{3}$$

where $\sigma^{\parallel}$ and $\sigma^{\perp}$ are, respectively, the cross sections for parallel and perpendicular polarizations of the lasers which, from Eq. (2), are given by

$$\sigma^{\parallel}=3\sigma_0^{\rm iso}+\tfrac{6}{5}\sigma_2^{\rm iso}, \tag{4a}$$

$$\sigma^{\perp}=\tfrac{3}{2}\sigma_1^{\rm iso}+\tfrac{9}{10}\sigma_2^{\rm iso}. \tag{4b}$$

Moreover, it is seen from Eq. (2) that at the "magic" angle for which $\cos^2\theta_m=\frac{1}{3}$ ($\theta_m\cong 54.7°$), $\sigma(\theta_m)=\sigma^{\rm iso}$, as previously pointed out by Siegel *et al.* [14] for the case of Ne($3p$) photoionization. Thus, to compare with theoretical cross sections calculated according to Eq. (1), we can either make the measurement at the magic angle, or measure $\sigma^{\parallel}$ and $\sigma^{\perp}$ and recombine them according to Eq. (3) with $\theta=\theta_m$; in fact, both methods of obtaining $\sigma^{\rm iso}$ were employed and excellent agreement was found. We note that this magic angle between the polarizations is not related to this specific case, but is a general property of electric dipole photoabsorption, just as in photoelectron angular distributions and polarization of fluorescence.

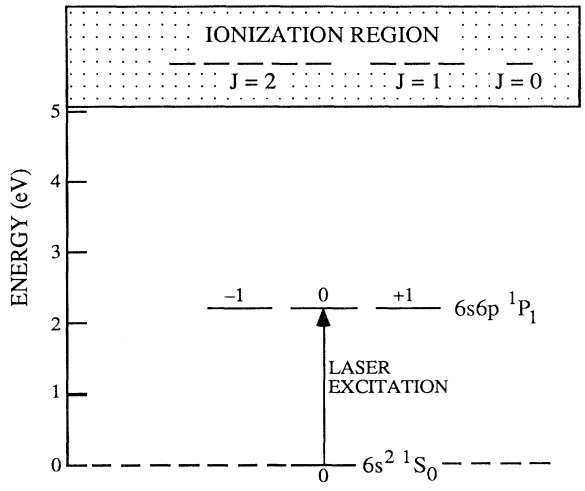

FIG. 1. Schematic diagram of the M_J sublevels of the states involved in the experiment. The $6s^2\ ^1S$ ground state has only $M_J=0$ while the $6s6p\ ^1P$ state has three sublevels as shown. The possible final states, both continuum and discrete states embedded in the continuum, may, because of the selection rules, have $J=0$, 1, or 2 as indicated. The excited state to be photoionized has only $M_J=0$ populated by laser excitation as shown because the laser light is plane polarized. The final-state sublevels that may be populated depend upon the angle between the polarization vectors of the two plane-polarized laser beams (see text).

Figure 2 shows our measured $\sigma^{\rm iso}$, acquired with $\theta=54.7°$, over the range 380–420 nm. Also shown for comparison are the results of the most recent theoretical results [10,11]. The ordinates in both figures are the absolute value of the cross section. Our method for determining this absolute value, which is an extension of a technique based on saturation of an ionizing transition, has been described previously [15,16]. In this work, the resonance near 390 nm (see Fig. 2) was used because it could be saturated, that is, all Ba $6s6p\ ^1P_1$ were ionized, by focusing the blue laser beam. If it is assumed that the laser beam is of uniform intensity, the total Ba^+ charge per laser pulse, Q, is given by

$$Q=eN_0V\left[1-\exp\left(-\frac{\sigma U}{2\hbar\omega A}\right)\right], \tag{5}$$

where e is the electronic charge, N_0 is the density of ex-

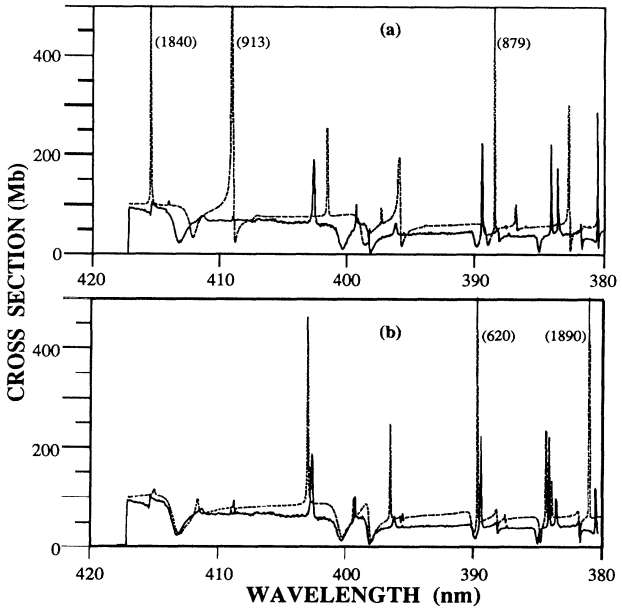

FIG. 2. Photoionization cross section of Ba $6s6p\ ^1P$ state near threshold. The solid lines are the data reported in this work. The dashed lines represent the calculations of (a) Ref. [10] and (b) Ref. [11].

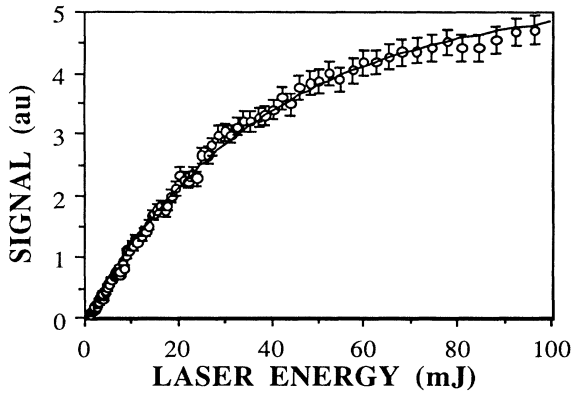

FIG. 3. Saturation curve used in the determination of the absolute value of the cross section. The data points were acquired at the strong resonance near 390 nm (see Fig. 2). The solid line represents our fit to these data as described in the text. The error limits on the data result from pulse-to-pulse fluctuations in the signal.

cited atoms, V is the interaction volume, A is the cross-sectional area of the laser beam, U is the total energy per ionizing laser pulse, $\hbar\omega$ is the energy per photon of the ionizing laser beam, and σ is the absolute cross section for photoionization. Thus, a measurement of Q as a function of U provides data which, when fitted by Eq. (5), yields the product N_0V and σ. It is important, however, to accurately measure both U and A.

The laser energy, which was measured with a calibrated pyroelectric detector traceable to the National Bureau of Standards and accurate to well within $\pm 5\%$, was varied using a gradient neutral-density-filter wheel. Both A and the intensity distribution across the beam were measured by scanning a pinhole across the focused laser beam. It was found that the intensity distribution is a strong function of the alignment of the optical system. Good alignment produces a nearly diffraction-limited laser spot with a relatively broad area of uniform intensity. For this condition, the fit by Eq. (5) is excellent. On the other hand, we found that poor alignment leads to hot spots and, as might be expected, a poor fit. Although our absolute measurements were acquired under the best alignment conditions possible, we nevertheless modified Eq. (5) to account for the Gaussian laser intensity distribution. The Gaussian width, the parameter replacing A in Eq. (5), is determined to within $\pm 10\%$. A typical saturation curve is shown in Fig. 3. The points are our data and the solid curve is the fit by the modified Eq. (5). The rms percentage deviation is $\pm 10\%$, which we consider to be a reasonable estimate of the overall error in the measurement. Based on these experimental uncertainties and several determinations of the absolute value of the cross section, we estimate our reported values to be accurate to $\pm 25\%$. The absolute values determined using this procedure were, however, reproducible to within $\pm 10\%$.

The outstanding feature of the comparisons in Fig. 2 is that the magnitude of the experimental and theoretical cross sections are in substantial agreement, in contradiction to the earlier measurement [12]. Furthermore, it is clear that no signal is seen below threshold, indicating that we are indeed measuring the photoionization cross section, unhampered by other ionization processes, in contrast to even the more recent measurement [17] from the laboratory of the authors of Ref. [12]. The details of the theoretical cross sections, particularly resonances, are seen to be in good qualitative agreement with our experimental results. Resonance positions appear to be predicted somewhat better by Ref. [11], but both calculations have some difficulty with a number of resonance heights and shapes. We note, however, that our results are in excellent agreement with a recent relative measurement [13], insofar as resonance positions and shapes are concerned. Of course, the theoretical situation is extremely complicated with Ba, since two electrons outside a closed shell are very highly correlated; additional complications result from relativistic effects in this heavy atom. Significant differences also exist between the two calculations shown. For example, for the resonance just above threshold Ref. [10] predicts a maximum of about 1800 Mb, while Ref. [11] shows only a minor feature. In addition, the structure at wavelengths shorter than 400 nm is quite different in the two cases.

Two groups [8–11] have reported R-matrix calculations of the photoionization of the Ba $6s6p\ ^1P$ state in which $6s$, $6p$, and $5d$ channels of Ba^+ were coupled. A

number of differences in the details of the calculations are evident, however. Among the differences are the following: The work of Refs. [8] and [10] used *ab initio* excited-state orbitals of Ba^+, while a semiempirical central field was used to generate these orbitals in Refs. [9] and [11]; in one calculation [8,10] spin-orbit effects were introduced via the Breit-Pauli Hamiltonian, while in the other [9,11] the spin-orbit Hamiltonian was used along with experimental energies; and one calculation [8,10] worked in the *jlK* coupling scheme, while the other [9,11] used *jj* coupling. Differences in the predictions of the two calculations are, thus, not unexpected.

The absolute cross section that had been measured and found to be in disagreement with theory by a factor of about 5 [9] has recently been remeasured by the same group [17]. Their revised value at threshold is now in rough agreement with theory and our measurement. We note, however, that their method of measuring the absolute cross section is substantially different than ours in that it depends upon the occurrence of atomic collisions, as evidenced by their signal below threshold, while ours strives to minimize any such effects. These workers also report resonances in the wavelength ranges 410–417 and 380–390 nm that seem to be consistent with our observations. Since, however, their experiment was performed with Ba ground-state density approximately 9 orders of magnitude higher than ours, and with laser power density considerably higher than ours (the $6s^2\,{}^1S_0 \rightarrow 6p'\,{}^3D_1^\circ$ resonance at 413.359 nm is prominent in their spectrum), comparison between their data and ours may not even be justified since their spectrum was produced by a combination of photoionization *and* at least two collisional ionization processes. Moreover, neither of their reports give information on the angle between the presumably linearly polarized laser beams so that comparison of their data with ours is inappropriate.

In conclusion, we have shown that an accurate absolute measurement of the photoionization cross section of the excited Ba $6s6p\,{}^1P$ state removes the huge discrepancy in magnitude between theory and experiment that existed. Our atomic-beam experiments also reveal the structure of the photoionization cross section near threshold, unobscured by collisional ionization processes. In addition, a general technique for measuring absolute cross sections for excited states is described. Furthermore, it was shown that different information is obtained by making measurements with the linear polarization vectors of the two laser beams set at various angles to each other. We have exploited a manifestation of the magic angle involving the relative orientation of the linear polarizations of the lasers which yields cross sections exactly the same as for *isotropic* excited states and pointed out the generality of this phenomenon. If we also make a measurement with two lasers circularly polarized in the same direction, only the $J=2$ final state is allowed. This, then combined with the present work, would allow determination of the individual cross sections for $J=0$, 1, and 2 final states, thus permitting a more detailed comparison with theory; this work is in progress and will be presented elsewhere, along with a discussion of the details of the resonances.

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