Measurement of Cross Sections for Electron Excitation out of the Metastable Levels of Argon

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We have measured electron excitation cross sections out of the $1s_3$ and $1s_5$ metastable levels of Ar into eight levels of the $3p^5 4p$ manifold. We use the optical method to determine the cross sections by measuring the radiation of the excited atoms. By optically pumping the $1s_5$ metastable atoms with a laser, we separate the contributions that each metastable level makes to our observed signal, and thus we can determine the excitation cross sections out of the individual metastable levels. We also interpret the trends in both magnitude and energy dependence observed for the cross sections. [S0031-9007(98)06582-X]

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This paper reports the first systematic experimental measurements for electron excitation cross sections out of the metastable levels of Ar. These cross sections are of great interest both for a fundamental understanding of atomic collisions and for a wide variety of gaseous electronics applications, ranging from gas discharge lasers to flat-panel displays to plasma-aided manufacturing [1–3]. In ionized gas applications, the plasma frequently has metastable densities that exceed 10^{-5} of the ground state density in the gas. The cross sections for electron excitation of metastable species into higher levels can be 100 or 1000 times as large as the corresponding cross sections for excitation of ground state atoms. In addition, electron temperatures in such systems are frequently low (less than a few eV). Thus there are orders of magnitude more electrons with sufficient energy for excitation out of the metastable levels ($\sim$1.5 eV for Ar) than there are with enough energy to excite atoms out of the ground state ($\sim$13 eV for Ar). This combination of low excitation threshold energies and large cross sections means that metastable atoms play a major or even dominant role in many low-temperature plasma properties including optical emissions [4,5], electron temperature [1,6], and both the ionization and energy balance [1,6]. Therefore cross sections for excitation out of metastable levels are essential for a quantitative description of the dynamics of ionized gas systems. Few experiments have been carried out on electron collisions with metastable atoms, and most of this work has been on helium [7]. The few measurements performed on metastable argon include cross section measurements of total electron scattering [8], ionization [9], and excitation [10,11]. Measurements of electron excitation cross sections out of the metastable levels of He exhibit numerous unexpected effects of fundamental interest [12,13]. The results reported in this Letter for excitation of metastable Ar will enable a more thorough understanding of electron-metastable atom collisions.

The first excited electronic configuration in Ar is $3p^5 4s$ (see Fig. 1). Of the four levels of this configuration, the $J = 0$ ($1s_3$ in Paschen's notation) and the $J = 2$ ($1s_5$ in Paschen's notation) levels are both metastable, with lifetimes over 1.3 sec. The next set of ten excited levels arise from the $3p^5 4p$ configuration ($2p_1$ through $2p_{10}$ in Paschen's notation). We present results for electron excitation out of both the $1s_3$ and $1s_5$ metastable levels into eight of the ten $2p$ levels using two different apparatuses.

The first apparatus is identical to the one that we have used to study electron excitation of metastable He [12]. Argon metastables are created in a hollow cathode discharge and then flow out of a 1 mm diameter hole in the base of the discharge, thereby forming a thermal atomic beam. The thermal atomic beam contains about 6×10^8 metastable Ar atoms/cm^3 and about 10^{14} ground level Ar atoms/cm^3 in the collision region. The atomic beam is crossed at an angle of 90° by a monoenergetic

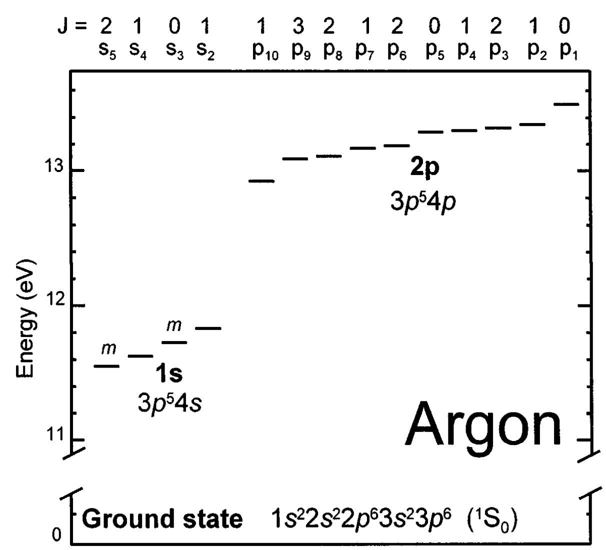

FIG. 1. Energy level diagram for Ar showing the first two excited configurations. The two metastable levels are indicated by the letter "*m*." The Paschen designation for each level is indicated at the top of the table, along with the corresponding value of *J*.

electron beam, and the resulting fluorescence is collected and analyzed with a narrow band interference filter and a photomultiplier tube.

The thermal beam contains metastable Ar atoms that are in both the $1s_3$ ($J = 0$) and $1s_5$ ($J = 2$) levels. The relative fraction of atoms in each metastable level is measured utilizing a laser-induced fluorescence technique [12]. A laser beam intersects the atomic beam and is used to pump the $1s_5$ or the $1s_3$ atoms into the same upper level. By measuring the resulting fluorescence, we have determined that the ratio of the number density of atoms in the $1s_5$ level to the $1s_3$ level is (5.6 ± 1.6):1. The same ratio has been obtained using both the $2p_2$ and $2p_4$ levels as the upper level into which the $1s_3$ and $1s_5$ atoms are pumped. Since the ratio of the number density of Ar metastables to the number density of the ground level atoms in the thermal atomic beam is 8×10^{-6}, this metastable beam target can be used only for electron excitation energies such that the ground level atoms are not excited into the 2*p* level being studied. Thus we obtain electron excitation cross sections only for energies less than about 11–12 eV from this beam source.

To study excitation at energies above ground state excitation onset we have a different apparatus that utilizes a fast beam of metastable atoms [14,15]. A radio-frequency ion source produces a 2.1 keV Ar ion beam, which passes through a cesium vapor target. There the Ar ions are converted into Ar atoms mostly in the four energy levels of the $3p^5 4s$ configuration ($1s_2$, $1s_3$, $1s_4$, $1s_5$) through the near resonant charge transfer reaction $\mathrm{Ar}^+ + \mathrm{Cs} \rightarrow \mathrm{Ar}(1s_2, 1s_3, 1s_4, 1s_5) + \mathrm{Cs}^+$ [16,17]. After deflecting away any remaining Ar ions and allowing the $1s_2$ and $1s_4$ atoms ($J = 1$) to decay to the ground level, the resulting fast beam is comprised of a mixture of atoms in the $1s_5$ and $1s_3$ metastable levels in a 5:1 ratio, along with an approximately equal number of ground level atoms [18]. The total metastable target density is about 10^5 atoms/cm^3. This fast beam target is then crossed by an electron beam at 90°. The fluorescence resulting from the electron excitation is detected with a photomultiplier tube and interference filter. This apparatus can be used for measurements of excitation cross sections for electron energies from 5 eV to approximately 1 keV. The method of absolute calibration for the apparatus involves measuring the ratio of the excitation signal out of the ground level (for which the cross section is known) to the excitation signal out of the metastable level. To obtain the results presented in this Letter, we utilized the ground level cross sections of Chilton *et al.* [19].

We have measured the $2p_9$ ($J = 3$) excitation signals at an electron energy of 10 eV with both the fast and the thermal atomic beam apparatuses. We use the fast beam measurements to absolutely calibrate the thermal beam experiment. The $2p_9$ ($J = 3$) cross sections obtained using this method have an absolute uncertainty of approximately 35%. The electron excitation cross sections for the other $2p$ levels are obtained by taking the ratio of their fluorescence signals to that of the $2p_9$ level. We utilize the ground level signals and cross sections to determine the optical efficiency of the apparatus at different wavelengths, as described by Piech *et al.* [12,13]. In this way we obtain absolute apparent electron excitation cross sections for the other *2p* levels. The fast beam experiment has also been used to obtain the absolute apparent cross section for the $2p_6$ level at 10 eV. The $2p_6$ cross section results from the fast beam experiment agree (within 5%) with the $2p_6$ cross section results from the thermal beam source obtained using the above mentioned ratio technique.

Using the thermal atomic beam apparatus we have measured the total fluorescence due to electron excitation of the mixed $1s_3$ ($J = 0$) and $1s_5$ ($J = 2$) metastable beam target into eight of the ten levels of the *2p* manifold. In order to differentiate between excitation of atoms in the $1s_3$ level from excitation of atoms in the $1s_5$ level, we quench the $1s_5$ atoms from the atomic beam target. We have used a laser (~500 mW and 2–3 GHz bandwidth) to remove the $1s_5$ metastable level atoms by pumping them into either the $2p_8$ ($J = 2$) or $2p_6$ ($J = 2$) level (Doppler width ~1 GHz). Atoms pumped into the $J = 2$ levels ultimately decay to the ground level through the $1s_2$ and $1s_4$ levels (both $J = 1$) but do not radiate to the $1s_3$ level ($J = 0$), so the $1s_3$ population remains unchanged. When the $1s_5$ metastables are completely quenched, the fluorescence from a particular *2p* level corresponds only to the $1s_3$ apparent excitation cross section into that particular *2p* level. The difference between the fluorescence from the unquenched beam and the quenched beam corresponds to the $1s_5$ excitation cross section into that *2p* level.

We present our cross section results in terms of the J value of the *2p* levels. Figure 2(a) shows the fluorescence signal of the $2p_9$ ($J = 3$) level with the quenching laser "on" and with the quenching laser "off." Since the fluorescence with the laser on is zero within our experimental uncertainty, it is clear that the excitation signal for the $2p_9$ is almost entirely due to excitation out of the $1s_5$ level. This also indicates that the $1s_5$ population is for all practical purposes completely quenched by the laser. The complete quenching has been observed to be valid over a wide range of laser powers. For the $2p_6$ ($J = 2$) excitation shown in Fig. 2(b), the fluorescence with the laser on is also nearly zero. We conclude that the fluorescence signal of the $2p_6$ level is also entirely due to electron excitation out of the $1s_5$ level. In general, however, the fluorescence signal is not solely due to excitation out of the $1s_5$ level. For example, for the $2p_4$ ($J = 1$) level [Fig. 2(c)], the difference between the fluorescence with the laser off and the laser on is only about 8%. This implies that most of the signal is due to excitation out of the $1s_3$ level.

The relative apparent cross sections are obtained as follows. At a given energy we measure the fluorescence with the laser off, S_{off}, and with the laser on, S_{on}.

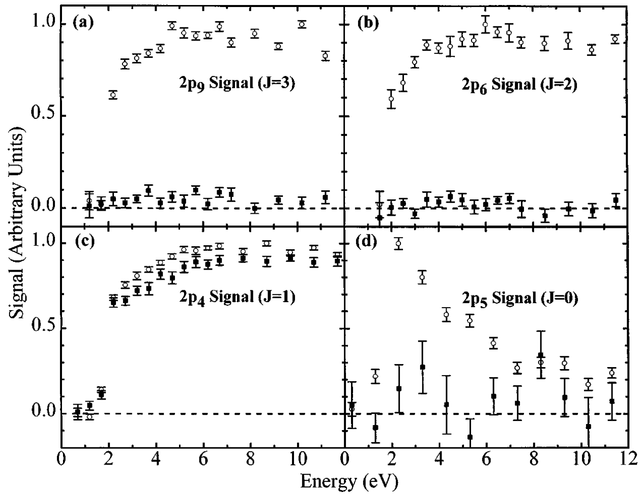

FIG. 2. (a)–(d) Observed fluorescence signal from $(1s_3, 1s_5) \rightarrow 2p_x$ electron excitation of metastable Ar. The open points (○) indicate the signal when the laser is off; the solid points (■) indicate the signal when the laser is on. The error bars shown represent the statistical uncertainty only, not any additional uncertainty from the absolute calibration.

We represent the $1s_3$ and $1s_5$ metastable target densities as n_{1s_3} and n_{1s_5}, respectively, and the corresponding metastable excitation cross sections as Q_{1s_3} and Q_{1s_5}. We then can express our signals as $S_{\text{on}} \propto Q_{1s_3} n_{1s_3}$ and $S_{\text{off}} - S_{\text{on}} \propto Q_{1s_5} n_{1s_5}$. We make these measurements as a function of the electron energy to obtain $1s_3 \rightarrow 2p_x$ and $1s_5 \rightarrow 2p_x$ excitation functions.

The fluorescence signals with the quenching laser on and off in Figs. 2(a)–2(d) illustrate several interesting points. First, there are two basic types of excitation function shape, those that are broad and slowly varying with energy ($2p_9$, $2p_6$, and $2p_4$), and those that vary rapidly as a function of the electron energy ($2p_5$). A second interesting feature is that the $2p_9$ and $2p_6$ excitations arise almost entirely from the $1s_5$ level, whereas the $2p_4$ excitation arises primarily from the $1s_3$ level. In general, we find that our measured cross sections for excitation out of the metastable levels of Ar into the 2*p* levels with $J = 1$, 2, or 3 are broad, slowly varying functions of the electron energy. For the $J = 0$ levels, we observe cross sections that are more rapidly varying functions of the electron energy. Table I shows the values of the apparent cross sections for eight of the 2*p* levels at two different energies. We have not yet measured cross sections for the $2p_7$ and $2p_{10}$ levels since the transitions out of these levels lie at unfavorable wavelengths for our detection system. The present results for the $2p_9$ level differ from our earlier results reported in Ref. [18]. The earlier work used the ground state cross sections of Ballou *et al.* [20] for absolute calibration, and these cross sections were not fully corrected for pressure effects. Recent measurements by Chilton *et al.* [19] have fully accounted for any pressure effects and were used to obtain the cross sections in Table I.

To obtain the direct cross section from the apparent cross section one must subtract off the cascade contribution. We are able to use the fast beam apparatus to place limits on the cascade cross sections for the $2p_9$ and the $2p_6$ levels. Because of the motion of the fast beam, an excited atom travels a significant distance between the point of excitation by the electron beam and the point where the atom decays. Thus the temporal dependence of the emissions is mapped into a positional dependence of the fluorescence which we measure by moving the electron beam relative to the detector. Emissions arising from *2p* atoms populated by cascades will have a different temporal (and thus spatial) pattern than emissions from *2p* atoms populated by direct excitation, enabling us to estimate the cascade contribution to the fluorescence. Using this technique, we have previously shown that the cascade cross section for the $2p_9$ level is much less than 20% of the apparent cross section [18]. We have now carried out similar measurements for the $2p_6$ level and have found that the cascade cross section is less than 10% of the apparent cross section. We expect the other large apparent cross sections of the *2p* levels to have similarly small cascade contributions.

We interpret the general trends of our cross section results as follows. The cross sections for excitations corresponding to dipole allowed optical transitions are usually large and have slowly varying energy dependence, and their magnitudes are qualitatively related to the oscillator strength of the transition. Thus, as observed in Fig. 2, we expect the excitations into the $J = 3$ and $J = 2$ levels to be primarily due to excitation out of the $1s_5$ ($J = 2$) level, since excitations out of the $1s_3$ level ($J = 0$) into levels with $J = 3$ or 2 do not satisfy the dipole selection rule. Excitation into the $J = 1$ levels can arise from both the $1s_3$ ($J = 0$) and the $1s_5$ ($J = 2$) levels. However, for the two $2p$ levels with $J = 1$ that we have been able to study ($2p_4$ and $2p_2$), the excitation arises primarily from the $1s_3$ level (see Table I). This is consistent with the oscillator strengths for the $1s_3 \rightarrow 2p_4$ and $1s_3 \rightarrow 2p_2$ transitions (0.53 and 0.31) being much larger than those for the $1s_5 \rightarrow 2p_4$ and the $1s_5 \rightarrow 2p_2$ transitions (0.003 and 0.028) [21]. For the two $J = 0$ levels ($2p_1$ and $2p_5$), the cross sections are found to be small and have a rapidly varying energy dependence. This can be explained by noting that the $J = 0$ levels are not optically connected to either of the $1s_3$ or $1s_5$ metastable levels, so excitation of these levels corresponds to dipole forbidden transitions. Excitations corresponding to dipole forbidden transitions typically exhibit sharper energy dependencies and smaller cross sections than excitations corresponding to optically allowed transitions [as seen in Fig. 2(d)].

Baranov *et al.* [10] and Mityureva *et al.* [11] have published results for excitation out of the metastable levels into the $3p^5 4p$ manifold. These results are strikingly

TABLE I. Apparent cross sections for excitation out of the $1s_3$ ($4s'[1/2]^o_0$) and $1s_5$ ($4s[3/2]^o_2$) metastable levels into the levels of the $3p^5 4p$ configuration. Entries with a $(\cdots)$ indicate that the fluorescence signal resulting from the given excitation amounted to less than 5% of the total signal observed. As a result, the magnitude of cross section for that excitation process was smaller than the uncertainty of the measurement. The uncertainty shown represents the uncertainty of the absolute calibration (±35%) plus any uncertainty from determining the relative signal from each transition.

		Apparent cross sections (10^{-16} cm^2)							
		$J = 0$		$J = 1$		$J = 2$			$J = 3$
Energy (eV)	Initial level	$2p_1$ $4p'[1/2]_0$	$2p_5$ $4p[1/2]_0$	$2p_2$ $4p'[1/2]_1$	$2p_4$ $4p'[3/2]_1$	$2p_3$ $4p'[3/2]_2$	$2p_6$ $4p[3/2]_2$	$2p_8$ $4p[5/2]_2$	$2p_9$ $4p[5/2]_3$
2.5	$1s_3$	<1.28	0.28 ± 0.19	8.54 ± 3.38	13.63 ± 5.63	⋯	⋯	⋯	⋯
10	$1s_3$	<0.85	<0.14	10.76 ± 4.26	18.79 ± 7.76	⋯	⋯	⋯	⋯
2.5	$1s_5$	0.15 ± 0.13	0.46 ± 0.16	0.36 ± 0.17	0.33 ± 0.17	1.14 ± 0.58	7.50 ± 2.67	5.62 ± 1.96	19.92 ± 6.93
10	$1s_5$	<0.09	0.13 ± 0.05	0.61 ± 0.26	0.24 ± 0.12	0.94 ± 0.48	8.86 ± 3.16	4.67 ± 1.73	23 ± 8.0

different from the results presented in this work. In general, their measured cross sections are about an order of magnitude larger than ours at 10 eV. The relative magnitudes and energy dependence of their cross sections also do not match the patterns that we have observed.

In summary, this paper has reported the first systematic experimental study of the electron excitation cross sections out of the metastable levels of Ar. It should be noted that the apparent electron excitation cross sections out of the $1s_3$ and $1s_5$ levels into the *2p* levels vary from about 500 times the magnitude of the corresponding excitation cross sections out of the ground level ($2p_4$) to 8 times as large as the corresponding ground level cross sections ($2p_1$). These cross sections show many interesting features that are crucial both for a fundamental understanding of atomic collisions and for gaseous electronics applications.

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