Autoionizing Rydberg series (np', nf') of Ar investigated by stepwise excitations with lasers and synchrotron radiation

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Synchrotron radiation is used to excite Ar to the intermediate states 3p_{1/2}^5 (3d'[3/2], 5a'[3/2], 5s'[1/2], 7s'[1/2]) and 3p_{3/2}^5 (6d[1/2], 6d[3/2], 8s[3/2]), then excited by lasers to the autoionizing Rydberg series 3p_{1/2} np' ((1/2)_{01}, (3/2)_{12}) and np'[5/2]_{12}. For the intermediate states of 5s', 7x', and 8s, the np' ((1/2)_{01} and (3/2)_{12}) series when the polarization vectors of two light beams are in parallel; but when they are in orthogonal, the np'[1/2]_{01} series disappears, the np'[3/2]_{12} intensity remains, and the np'[1/2]_{01} and (3/2)_{12} series show up strongly. The intensity distribution of the np' series strongly depends on the intermediate state. The spectra of the np' series are assigned according to their intensity variation with the polarization vectors. The quantum defects determined for the series np'[1/2]_{01}(n=11–57), np'[3/2]_{12}(n=11–65), np'[3/2]_{12}(n=11–31), and nf'[5/2]_{12}(n=9–74) are 1.611 ± 0.011, 1.683 ± 0.013, 1.688 ± 0.010, and 0.016 ± 0.005, respectively. Our values are in excellent agreement with theoretical prediction. The spectral line shapes of autoionizing Rydberg states are analyzed with a Beutler-Fano profile. Reduced autoionization linewidths for the np'[1/2]_{01}(n=11–16) series vary in the range 2549–4145 cm⁻¹, and the nf'[5/2]_{12}(n=9–11) series in 186–247 cm⁻¹ in reasonable agreement with theoretical prediction.

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I. INTRODUCTION

The odd-parity Rydberg series of Ar (ns, ns', nd, and nd') have been extensively investigated [1–3], but the even-parity series of np, np', nf, and nf' are not well known. The odd-parity series can be reached by optical excitation of Ar in the ground state 3p_{6}^1S_0 but the even-parity series are optically forbidden by single-photon excitation so that they can be accessed only via the excited odd-parity Rydberg states. Because excited intermediate state atoms are difficult to prepare, to investigate the even Rydberg series is a challenging task. Stepwise excitation, preparing odd-parity Ar⁺ atom by synchrotron radiation (SR) and then exciting it to an even-parity state by a laser, is an elegant way to do such a study. Here we report an extensive study on the even-parity autoionizing Rydberg series (ARS) with this technique.

In 1970, Yoshino [4] observed some weak even Rydberg series from excitation of Ar in the ground state, but these series are limited to the members below the first ionization threshold. High-energy members are hidden under strong absorption continua that resulted from direct photoionization of the Ar and Ar₂ dimer. Later, Dunning and Stebbings [5,6] observed some ARS between the first and second ionization thresholds (9 < n < 26) by ultraviolet excitation of metastable Ar (3P_0)⁺ atoms generated from electron-impact excitation of Ar (3p_{6}^1S_0). They reported that every series member has only one single peak. In 1995, Koeckhoven et al. [7] observed some ARS in the same n range using four-photon excitation of Ar in the ground state. In their spectra, the np' [1/2]_{01} and np'[3/2]_{12} series were unresolved, in contrast to those of Kr and Xe that were well resolved. Based on observation of a single peak, Petrov et al. [8,9] assumed that the np'[1/2]_{01} and [3/2]_{12} states have the same resonance width in their calculation; their theorized linewidth turns out to differ from the experimental value by one order of magnitude. Further experimental measurements to test their calculation are clearly needed.

In 2005, Peters et al. [10] investigated the np' series by uv excitation of metastable Ar (3p_{5}^4s^2P_2) atoms produced by electrical discharge; they observed the 14p' member with a resolved structure. They expected that the 14p' member has three states: [3/2]_{2}, [3/2]_{1}, and [1/2]_{1}, but only two lines were barely resolved [10]. By comparing the observed absorption line shape with theoretical calculation, they assigned the observed broad line to 14p' [1/2]_{1}. Although the linewidth of 14p' [1/2]_{1} agrees reasonably well, the linewidths of transitions to the [3/2]_{2} and [3/2]_{1} states are sharp in contrast to the calculated results. They attributed the disagreement to a lack of instrumental resolution. Better measurements of the linewidths and energies of these two states
are needed to verify their theoretical calculations.

Recently, Petrov et al. [11] calculated the absorption cross sections to the four 14p (3/2), 5d (3/2), 5s (1/2), and 7s (1/2) states by optical-excitation from an initial state, 3s or 4s. They found that the absorption cross sections vary dramatically with the initial state; that is, the transition dipole moment strongly depends on the initial state. It is of interest to verify their calculation experimentally.

It is well established that stepwise-excitation experiments with a combination of SR and lasers provide an opportunity to obtain new scientific information [12–16]. SR has the advantage of ready accessibility and broad tunability in the high-energy photon region, and lasers have high intensity and high resolution. In a “pump-probe” experimental scheme, a SR beam serves to populate a selected and well-defined intermediate state that is subsequently examined with a laser beam. Using this technique, we can investigate various physical aspects of excited states that are forbidden to one-photon excitation by dipole selection rule.

All the states relevant to the current study are depicted in Fig. 1. The intermediate states are 3p1/2 (3d' [3/2], 5d' [3/2], 5s' [1/2], 7s' [1/2]), and 3p3/2 (6d [1/2], 6d [3/2], 8s [3/2]), and the ARS are 3p1/2 np' ([1/2], [1/2], [3/2], [5/2]), and nf' (5/2). Following the selection rules, the number of accessible states is limited; hence the ARS spectra are relatively simple and easy to analyze. We investigate the Rydberg series up to very high n members that are unreported.

II. EXPERIMENTAL

The experimental setup has been described elsewhere [16]. The experimental apparatus was comprised of two light sources and a vacuum chamber, containing a molecular beam source and a photoionization mass spectrometer [17], as shown in Fig. 2. A noble gas beam (400 Torr) was expanded through a nozzle (diameter 100 μm), skimmed into the interaction chamber and crossed with counterpropagating synchrotron radiation and laser beams in the ion-extraction region of a quadrupole mass filter (QMF) tuned at mass 40. The main chamber was typically operated at a pressure less than 3 × 10⁻⁷ Torr.

FIG. 1. Two-photon excitation scheme of Ar relevant to current investigation.

FIG. 2. Schematic experimental setup.
The SR was provided by the high-resolution monochromatic beamline (BL.21B2) equipped with cylindrical gratings that select photons in the energy range of 6–120 eV with resolving power of $E/\Delta E > 10^5$ [18]. The slit width was set at 50 μm that gave a resolving power $\sim 2 \times 10^4$ at 15 eV, e.g., the resolution was about 6 cm$^{-1}$. Only a small fraction of light within the resonance line width of an intermediate state (in the order of 0.01 cm$^{-1}$) is absorbed. Near-infrared radiation was produced from a Ti:sapphire laser or an optical parametric oscillator (OPO) that propagated in a direction opposite to the SR and was mildly focused to a spot of diameter $\sim 0.5$ mm to match with the SR beam at the QMF ion-extraction region. The wavelength of the Ti:sapphire laser was measured by a wavemeter with an accuracy of 0.02 cm$^{-1}$. By rotating a birefringent filter with a computer-controlled linear actuator, the Ti:sapphire laser energy is tunable from 11690–13870 cm$^{-1}$ (1.45–1.72 eV); its highest output power is 750 mW and its spectral width is $\sim 0.25$ cm$^{-1}$. The laser output is linearly polarized with an axial ratio greater than 300. The laser polarization is rotatable with a half-wave Fresnel rhomb polarizer. The laser was operated in the cw mode in this experiment.

For probing the high $n$ members of ARS, a midinfrared OPO was implemented as the ionization source. The light source was a grazing-incidence periodically poled lithium niobate OPO similar to those described in previous reports [19,20]. This OPO laser is capable of producing more than one hundred milliwatts of infrared power in a bandwidth of 0.1 cm$^{-1}$ in the 1.4–3 μm region. Continuous fine scanning was accomplished by rotating a mirror in the OPO cavity with a microstepping motor attached to a micrometer, controlled by a computer. The scanning range for the full width at half-maximum (FWHM) power at a single temperature and a crystal grating period was $\sim 30$ cm$^{-1}$ [21]. Two concave gold-coated copper mirrors were used to focus the infrared beam into one of the two identical resonator tubes of a differential photoacoustic (PA) detector used for wavelength calibration of the OPO laser. The PA signal from H$_2$O or 200 ppmv of methane in nitrogen at 760 Torr and 25 °C [22] was measured with a phase-sensitive lock-in amplifier (SRS; Model 830) and recorded with a computer. The signal was plotted as a function of the motor step to obtain a PA spectrum. The spectrum was then displayed and calibrated with that of HITRAN [23] to provide the infrared (ir) wavelength.

III. RESULTS

A. Intermediate state 3$p^{5}_1^{1/2}5s'[1/2]_1$

The photoionization spectrum produced via first excitation with SR to the intermediate state 3$p^{5}_1^{1/2}5s'[1/2]_1$ at 114975.02 cm$^{-1}$ [3] and then excited by a Ti:sapphire laser at varied photon energies is shown in Fig. 3. The abscissa denotes the wavenumber sum of the laser photon and the intermediate state. The intensity is in arbitrary units. In Fig. 3(a), the polarization vectors of two light beams are in parallel. The ARS positions for 3$p^{5}_1^{1/2}$ (np$'$ [1/2]$_0$), np$'$ [3/2]$_2$ and nf$'$ [5/2]$_2$) are indicated. For $n<16$, the peaks for every np$'$ [1/2]$_0$ and [3/2]$_2$ pair is resolved; but at higher $n$, they are unresolved limited by the bandwidth of Ti:sapphire laser, but the structure is resolved using the OPO laser (see the spectra shown later). The intensities of the np$'$ [3/2]$_2$ state are weaker than those of np$'$ [1/2]$_0$ for $n=11, 12, 14$, and they are reversed for $n=13$ and 15. The intensity of the np$'$ series is quite strong compared with those of the np$'$. When the angle, $\theta$, between the polarization vectors of two light beams is rotated to 90°, the np$'$ [1/2]$_0$ series disappears, but the np$'$ [3/2]$_2$ and [1/2]$_1$ series show up as shown in Fig. 3(b). The intensity of the np$'$ [5/2]$_2$ series is relatively intense compared with those of the np$'$ [3/2]$_2$ and [1/2]$_1$ series. The np$'$ [3/2]$_2$ and [1/2]$_1$ series are not optically allowed at $\theta=0°$, but they become allowed at $\theta=90°$. Since the np$'$ [5/2]$_2$ state is optically forbidden for transition from
the intermediate state \( s' \) state but allowed from \( d \) and/or \( d' \) states, the intense \( nf' \) series shown in Fig. 3(b) may indicate that the 5s state is mixed with \( d \) and/or \( d' \) character. The \( nf' \) series may also result from the Coulomb interaction between the Rydberg electron and the core electrons.

As shown in Fig. 3(a), the ion signal starts to appear at the total energy of 127078 cm\(^{-1} \) (15.7556 eV), which is about 32 cm\(^{-1} \) below the first ionization potential of Ar. Similar low thresholds for the Ar\(^{+} \) appearance were reported by Koekhoven et al. [7] and Radler and Berkowitz [24]; this is accounted for by the effect of electric field constantly applied in the QMF ion-extraction area. The electric field will induce collisional ionization of high-\( n \) Rydberg atoms below the ionization limit [7,24]. The dependence of the first Ar ionization potential on electric field has been systematically studied by Merkt [25] with a zero-kinetic-energy photoelectron-spectrum technology. Assuming that the first ionization potential of Ar is linearly dependent on electric field, the observed ion-signal threshold implies that the electric field in the QMF ion-extraction region is about 8 V/cm. This is consistent with the value estimated from the voltage applied in that region. The effect of electric field on the ARS of Ar is systematically investigated by Fielding and Softly [26]. Their results indicate that the electric field in our experiment is too low to disturb the angular momenta of the core and Rydberg electron as well as total angular momentum. At high electric field, for example, \( \geq 100 \) V/cm, additional side-bands may appear nearby the ARS states [26], which do not show in our spectrum, indicating that our spectra are not distorted by the applied electric field.

**B. Intermediate state \( 3p_{1/2}^57s'[1/2]_1 \)**

The spectrum produced via the state \( 3p_{1/2}^57s'[1/2]_1 \), of energy 123882.203 cm\(^{-1} \) [3] is shown in Fig. 4, where the OPO laser was used. For OPO laser experiments, there is no electric field in the QMF ion-extraction region during optical excitation period so that the spectra are free from possible electric field distortion. Figure 4(a) shows the spectrum observed at light-polarization vectors in parallel. The positions of the \( 3p_{1/2}^5np' [(1/2)_0 \) and \( (3/2)_0 \) \) states for \( n=28–70 \) and the \( nf'(5/2)_2 \) state for \( n=26–36 \) are indicated. The structure for the \( np' [(1/2)_0 \) and \( (3/2)_0 \) \) pair is well resolved, because the OPO laser has a high resolution. The intensity of the \( [1/2]_0 \) state is much weaker than that of \([3/2]_0 \), differing from those shown in Fig. 3(a). The intensities of the \( nf'(5/2)_2 \) series are also relatively weak in comparison to that of \( np' \), implying that the 7s' \) state mixes little with the \( d \) and/or \( d' \) states, or the interaction between the Rydberg electron and the core electrons is weak.

When the polarization vectors were rotated to perpendicular, the spectrum varies significantly as shown in Fig. 4(b). There are two series appear at energy slightly below the \([3/2]_0 \) as shown in the expanded inset of Fig. 4(b). These series are attributed to \( np' [3/2]_0 \) and \( [1/2]_0 \), which become electrically allowed when the polarization vectors are orthogonal. It is noted that the intensity of the \( np' [1/2]_0 \) series is weak in both spectra of Fig. 4, when \( \theta \) varies from 0 to 90°. This differs from the case of the 5s' \) state where the intensity the \( np' [1/2]_0 \) series changes greatly as shown in the two spectra of Fig. 3.

As shown in Fig. 4, there are three additional bands at 128391.57, 128424.97, and 128505.20 cm\(^{-1} \). These bands are quite broad when compared with the ARS bands. They may be produced by photodissociation of Ar\(^{+} \) and/or Ar\(^{+} \) dimer excited in Rydberg states, a subject of further investigation in the near future.

**C. Intermediate state \( 3p_{3/2}^58s[3/2]_1 \)**

The spectrum produced via the state \( 3p_{3/2}^58s[3/2]_1 \) at 123935.87 cm\(^{-1} \) [3] is shown in Fig. 5. The spectrum taken...
with the polarization vectors of two light beams in parallel is shown in Fig. 5(a), where the OPO laser was used. The positions for the $3p_{1/2}^3 np'' [1/2]_0$ and $[3/2]_2$ and $n\ell'' [5/2]_2$ states are indicated. In the spectrum, the intensity of the $[1/2]_0$ state is greater than that of $[3/2]_2$, in contrast to those of $5s'$ and $7s'$ shown in Figs. 3 and 4, respectively. The $\ell''$ series is quite strong when compared with $np'$, indicating that the $8s$ state has a $d$ and/or $d'$ character, or the interaction between the Rydberg electron and the core electrons is strong.

When the polarization vectors are orthogonal, the intensity of the $[1/2]_0$ state deceases, but those of $np'' [3/2]_1$ and $[1/2]_1$ become intense as shown in Fig. 5(b). To find out the reason for such a dramatic variation of intensities is of interest and it is explainable by theoretical calculation that will be further discussed later. Again, two broad bands appear in the spectra at positions 128445.63 and 128487.81 cm$^{-1}$, that may be from Ar$_2^+$ and/or Ar$_2^*$. It is noted that the background signal shown in Fig. 5 is much stronger than those of $5s'$ and $7s'$ shown in Figs. 3 and 4, respectively. The larger background signal may be because of the intermediate state $3p_{1/2}^3 8s [3/2]_2$, which has a core configuration similar to the first ionic state Ar$^+ (2P_{3/2})$, so that it can be more easily direct-photoionized into Ar$^+$ than the $3p_{1/2}^3 ns' [3/2]_2$ states that have a different ionic core.

D. Intermediate state $3p_{1/2}^3 3d' [3/2]_2$

The $\ell'' [5/2]_2$ series appear up in the spectra shown in Figs. 3–5, which are attributed partly to the mixture of the $s$ and $s'$ states with the $d$ and/or $d'$ states; it is of interest to prove this possibility. The spectra produced via the $3p_{1/2}^3 3d' [3/2]_2$ state at 115366.866 cm$^{-1}$ [3] combined with a Ti:sapphire laser are shown in Fig. 6. The spectrum taken with two polarization vectors in parallel is shown in Fig. 6(a), which is similar to the one shown in log scale in a previous
paper [16]. The positions of the $3p_{1/2}^5 np' [1/2]_0$ and $np' [3/2]_2$ and $nf' [5/2]_2$ states for $n=9–23$ are indicated. The intensity of the $nf'$ series is indeed about two orders of magnitude intense than those of $np'$. Although the $np'$ series are optically allowed for transition from the intermediate state $3p_{1/2}^5 3d'[3/2]_1$, their intensities are relatively weak. The larger intensity of the $nf'$ series is explainable by the fact that its wave extends to a large distance from the core so that it has a better overlap with the Rydberg electron wave. It is noted that the intensity of $3p_{1/2}^5 np'[1/2]_0$ is much intense than that of $np' [3/2]_2$.

The spectrum taken at the polarization vectors of two light beams in perpendicular is shown in Fig. 6(b). The intensity of the $nf'$ series remains, but the intensity of $np' [1/2]_0$ is greatly reduced and the intensities of $np' [1/2]_1$ and $[3/2]_1$ increase.

**E. Intermediate state $3p_{1/2}^5 5d'[3/2]_1$**

The spectra produced via the state $3p_{1/2}^5 5d'[3/2]_1$ at 123815.56 cm$^{-1}$ [3] combined with the OPO laser are shown in Fig. 7, where the polarization vectors of two light beams are (a) parallel and (b) perpendicular. The positions of the $3p_{1/2}^5 np' [1/2]_0$ and $np' [3/2]_2$ and $nf' [5/2]_2$ states for $n=25–60$ are indicated in (a) and those of $np' [3/2]_1$ and $[1/2]_1$ for $n=27–50$ in (b). The intensity distributions of these two spectra are similar to that of the $3d'$ intermediate state as shown in Fig. 6, except the $n$ members are much higher. These spectra are used to determine the quantum defects of high $n$ members of the $nf'$ series.

**F. Intermediate state $3p_{3/2}^5 6d' [1/2]_1$ and $[3/2]_1$**

The spectra produced via $3p_{3/2}^5 6d'[1/2]_1$ at 123467.9733 cm$^{-1}$ and $3p_{3/2}^5 6d'[3/2]_1$ at 123997.01 cm$^{-1}$ states [3] combined with the OPO laser are shown in Fig. 8(a) for $n=28–58$ and in Fig. 8(b) for $n=45–70$, respectively, where the polarization vectors of two light beams are in parallel. The intensity distribution of these spectra are similar to those produced by other $nd'$ states; the spectra are all dominated by the $nf'$ series. However, it is noted that the continuum background signal produced by this $6d$ intermediate state is much higher than those of $nd'$. Again, this may be explainable by the fact that the $3p_{1/2}^5 6d$ state has the same core configuration as the first ionic state, $Ar^+(p_{1/2}^4)$, so that it has an ir photoionization cross section greater than those of the $3p_{1/2}^5 nd'$ states.

**G. Dependence of intensity on $\theta$**

All the above spectra show that the relative intensities among the four $np'$ series depend strongly on $\theta$, the angle between the polarization vectors of two light beams. To further illustrate this effect, the spectra of the $11p'$ states produced via the $3p_{3/2}^5 3d'[3/2]_1$ state at angles $\theta=0^\circ$, $20^\circ$, $40^\circ$, $60^\circ$, $80^\circ$, and $90^\circ$ are shown in Fig. 9. At $\theta=0^\circ$, an intense line for the $11p' [1/2]_0$ state appears at 127295.9 cm$^{-1}$, a weak line for $11p' [3/2]_1$ at 127278.5 cm$^{-1}$, and a very weak line for $11p' [3/2]_2$ at 127275.8 cm$^{-1}$. When $\theta$ increases, the intensity of the $[1/2]_0$ state decreases, and that of $[3/2]_1$ increases significantly; also, the $[1/2]_1$ state shows up as a broad feature with a peak position between the $[3/2]_1$ and $[3/2]_2$ lines. The intensity of the $[3/2]_1$ reaches maximum at $\theta$ near $90^\circ$, but the $[1/2]_0$ state systematically decreases to very small at $\theta=90^\circ$. It is noted that the intensity for $[3/2]_2$ is independent of $\theta$.

According to the $j,K$-coupling principle that is generally applicable for rare gases and high $n$ members, there are four states for an $np'$ member, $3p_{1/2}^5 np' ([1/2]_0, [1/2]_1, [3/2]_1$ and $[3/2]_2)$ [11,27,28] accessible from the current studied intermediate states. When $\theta=0^\circ$, the $np' ([1/2]_0$ and $[3/2]_2)$ states are optically allowed, but not $np' ([1/2]_1$ and $[3/2]_1)$. Transitions to these two $J=1$ states are optically forbidden because their transition moments contain a momentum factor.
that is equal to zero [28,29]. This selection rule is obeyed as shown in Fig. 9 at $\theta=0^\circ$, where the intensity for the $J=1$ states is almost zero. When the polarization vectors of the light beams are orthogonal, the final states must have $M_J=\pm1$ so that the $np^\prime \ [1/2]$ state is not accessible [28]. In Fig. 9, when the polarization angles rotate from $0^\circ$ to $90^\circ$, the intensity of the $[1/2]$ state deceases from a maximum to almost 0. (The small nonzero intensities for the $J=0$ states at $\theta=0^\circ$ and the $J=0$ state at $\theta=90^\circ$ may be caused by the imperfect light polarizations and/or the alignment between the light beams; the small nonzero intensities in turn show that the experimental condition is very good.) From the experimental spectra of Figs. 3–7 and 9, we conclude that the selection rules are generally followed.

IV. DISCUSSION

The experimental results show that the ARS spectra vary greatly with intermediate states and polarization angles. Based on selection rules and recent detailed theoretical calculations [8–11], our observed ARS positions can be assigned with great certainty. Also, our experiment provides autoionization-decay widths and quantum defects that can be used to compare to calculations and thus to verify theory.

A. Assignment for the $np^\prime$ series

The photoabsorption cross section for the $4s^\prime[1/2], 14p^\prime$ transition has been calculated by Petrov et al. [11] that is copied in Fig. 10(a) to compare with our observation.

FIG. 8. Two-photon ionization spectra produced via the intermediate states (a) $3p_{1/2} 6d \ [1/2]$, and (b) $3p_{1/2} 6d \ [3/2]$, denoted as $6d1$ and $6d3$, respectively. The abscissa denotes a wavenumber sum of the OPO laser and the intermediate state. The polarization vectors of two light beams are in parallel. The transitions to the $3p_{1/2} np^\prime \ [(1/2)_{0}$ and $[3/2)_{2}]$ and the $3p_{1/2} n_f^\prime \ [5/2]_{2}$ states are indicated in (a), and the $3p_{1/2} (np^\prime \ [1/2]_{0}$ and $nf^\prime \ [5/2]_{2}$) states in (b).

FIG. 9. Two-photon ionization spectra produced via intermediate state $3p_{1/2} 3d^\prime \ [3/2]$. The abscissa denotes a wavenumber sum of the Ti:sapphire laser and the intermediate state. The angles between the polarization vectors of two light beams vary from $0^\circ$ to $90^\circ$ as indicated. The positions of the $3p_{1/2} np^\prime \ [(1/2)_{0}, [1/2]_{0}, [3/2]_{2}$, and $[3/2]_{2}$] states are indicated.
on the 5s'[1/2] → 14p' transition at θ = 0° in Fig. 10(b). Accordingly the broad line is assigned to the 14p'[1/2], the sharp one to 14p'[3/2], and the weak lines to 14p' ([1/2]l and [3/2]l). The calculated position for the sharp line agrees well with the observed one, but the broad line has a larger calculated value of 0.2 meV (∼1.6 cm⁻¹). The variation may be partly caused by different intermediate states (4s' vs 5s'). Absorption cross section depends on the transition dipole moment connecting the intermediate state to the np' states, it can thus be affected by intermediate state. The predicted weak line is not observed, but similar lines are observed in other spectra, for example, for 4s'[1/2] → 14p' in Fig. 10. In general, although there are some differences, the calculated and observed spectra do have a good agreement. The agreement implies that the assignment [11] for the positions of the np' series is reliable, which is adopted to analyze in all spectra observed.

As shown in Fig. 10, the observed band shape of 14p'[1/2], agrees well with theoretical calculation, but that of 14p'[3/2] is broader. The difference is likely caused by the large Ti:sapphire laser bandwidth of ω_laser ∼ 0.25 cm⁻¹. The actual line width can be obtained from the observed one by deconvolution over the laser bandwidth with an assumption of Gaussian line shape [1,2]

$$\omega_{\text{obs}}^2 = \omega_{\text{line}}^2 + \omega_{\text{laser}}^2.$$  

From our observed width of ω_obs = 0.71 cm⁻¹, the actual linewidth is ω_line = 0.66 cm⁻¹, about twice larger than the calculated one [11].

B. Compare calculated cross section with measurement

The photoabsorption cross sections for the 4s'[1/2] and 4s'[1/2] → 14p' transitions are computed by Petrov et al. [11] as copied in Figs. 11(a) and 11(b), respectively. They calculated the cross sections with (solid line) and without (dashed line) taking the virtual 4p shell into account. The spectra we select for comparison purposes are the 28p' states produced via two intermediate states 3p'^5 7s'[1/2] and 5p'^5 8s[3/2], which are shown in Figs. 4 and 5 and replotted in an expanded scale in Figs. 11(c) and 11(d), respectively. (It is noted that the n number is different from the theoretical one because of the availability of our data. At

FIG. 10. (a) The spectrum calculated for the transitions 3p'^5 4s' [1/2] → 3p'^5 14p' [1/2], [1/2]l, and [3/2]l (adopted from Fig. 3 in Ref. [11]). (b) Two-photon ionization spectrum of Ar[3p'^5 14p'([1/2]l and [3/2]l)] produced via the intermediate state 3p'^5 5s' [1/2]l, denoted as 5s'. The abscissa denotes the energy scale referred from the second ionization potential. The polarization vectors of two light beams are parallel.

FIG. 11. The spectra calculated for the transitions (a) 4s' (J_o=1) → 14p' and (b) 4s' (J_o=1) → 14p' (adopted from Fig. 4 in Ref. [11]). Two-photon ionization spectra of Ar[3p'^5 28p'] produced via (c) the 3p'^5 7s' [1/2]l, and (d) the 3p'^5 8s [3/2], denoted as 7s'1 and 8s3, respectively. The abscissa denotes a wave-number sum of the OPO laser and the intermediate states. The polarization vectors of two light beams are in parallel.
perpendicular.

especially, the large intensity of virtual 4\( \text{p} \) is shown in Fig. 11, denoted as 7s'1 and 8s3, respectively, are observed when the polarization vectors of two light beams are perpendicular.

different \( n \) numbers, the spectra will vary in detail, but their common shape and structure may be preserved. Therefore, although the comparison is not vital, it will provide a reasonable cross-check for theoretical calculation.) The calculated curves shown in Figs. 11(a) and 11(b) are compared with our spectra shown in Fig. 11(c) and 11(d), respectively. This comparison indicates that the calculation without taking the virtual 4p shell into account agrees better with our data. Especially, the large intensity of [1/2]\( \text{p} \) shown in Fig. 11(d) agrees with the dash line in Fig. 11(b), concluding that the calculation without taking the virtual shell into account is more favorable. Further theoretical calculations on the np' spectra are of interest.

C. Spectral dependence on intermediate state and polarization angle

The spectra of the np' series are affected by intermediate states and polarization angles as shown in Figs. 3–8. This effect is further illustrated in detail in Figs. 12(a)–12(d), where the 28p' spectra are produced via 5d'\( [3/2]_1 \), 7s'\( [1/2] \), and 8s\( [3/2] \), respectively. Figures 12(a) and 12(b) show the spectra produced via 5d'\( [3/2]_1 \) at \( \theta=0^\circ \) and 90°, respectively. As we know, the intensity of [1/2]\( \text{p} \), decreases when \( \theta \) rotates from 0° to 90°, and the intensity of [3/2]\( \text{p} \) does not depend on \( \theta \). Comparing the spectra produced via 7s' and 8s at \( \theta=90^\circ \), as shown in Figs. 12(c) and 12(d), with those at \( \theta=0^\circ \) in Figs. 11(c) and 11(d), we find that the intensity ratio of the [1/2]\( \text{p} \) and [3/2]\( \text{p} \) states changes with \( \theta \). From these spectra observed, it is conclusive that although the np' spectra vary in detail, the common structures are generally preserved for varied intermediate states and polarization angles.

D. Confirm spectral assignment by polarization effect and linewidth

From the spectra in Figs. 9–12, it is clear that the ARS intensity distribution depends on the polarization angles, and the spectral intensity obeys selection rules. In summary, the np'\([1/2]_0 \) has a maximum intensity at \( \theta=0^\circ \) and a minimum at 90°; the intensity of the np'\([3/2]_2 \) is not affected by varying \( \theta \); and the intensities of both the np'\([3/2]_2 \) and [1/2]\( \text{p} \) series increase with increasing \( \theta \). This polarization effect can in turn be applied to confirm the assignment of the ARS states without ambiguity.

In addition to the polarization effect, the spectral assignment can also be cross-checked by comparing the calculated line width with the one observed. For instance, Petrov et al. [11] calculated that the linewidth of the np'\([1/2]_0 \) state is about the same as that of [1/2]\( \text{p} \), but that of [3/2]\( \text{p} \) is about one order smaller. This confirms the assignment of the sharp peak at 12725.74 cm\(^{-1} \) shown in Fig. 9 to the 11p'\([3/2]_2 \) state and the broad band underneath to 11p'\([1/2]_0 \).

E. Spectral assignment of the nf' series

Based on the j,K-coupling principle [22], a 3p'\( [5/2]_0 \) Rydberg member contains four states \([7/2]_1 \), \([7/2]_3 \), \([5/2]_3 \), and \([5/2]_1 \). With the intermediate states 3p'\( [5/2]_0 \)\( 3d'[3/2]_1 \) and 5d'\([3/2]_1 \) and 3p'\( [5/2]_0 \)\( 6d[3/2]_1 \) studied in current experiment, only the 3p'\( [5/2]_0 \)nf'\([5/2]_1 \) series can be accessed by laser excitation. Since this series has only a single component, it is easy to identify as shown in Figs. 6–8. The nf'\([5/2]_1 \) series is also produced via the 3p'\( [5/2]_0 \)\( 5s'[1/2] \) intermediate state as shown in Fig. 3; this is likely caused by the mixture of 5s' with the nearby 3p'\( [5/2]_2 \)\( 3d'[3/2]_1 \) state, and/or a strong interaction between the Rydberg electron and the core electrons. The nf'\([5/2]_2 \) series produced via the 3p'\( [5/2]_1 \)\( 7s'[1/2] \) and 3p'\( [5/2]_0 \)\( 8s[3/2] \) intermediate states are, however, quite weak as shown in Figs. 4 and 5, respectively.

Since the nf' state is single and well isolated, it is ideal for studying the dependence of intensity on polarization angle and intermediate state. As an example, the spectra of nf' produced via the 3p'\( [5/2]_1 \)\( 3d'[3/2]_1 \) and 3p'\( [5/2]_3 \)\( 3d[3/2]_1 \) states are shown in Fig. 13. The line shapes produced via the 3d' state shown in Figs. 13(a) and 13(b) for \( \theta=0^\circ \) and 90°, respectively, are about the same; that is, the line shape does not depend on the polarization angle. In general, the line shapes of the nf' series produced via the 3d' and 5d' intermediate states are not affected by polarization angle.

The spectrum produced via the 3p'\( [5/2]_1 \)\( 3d[3/2]_1 \) intermediate state that was published in a previous paper [16] has a Beutler-Fano profile as shown in Fig. 13(c). This shape is

![Figure 12](image-url)
ground state so that it can be easily ionized by ir laser; this is produced via the intermediate state $3d'[3/2]_2$, denoted as $3d'3$, when the polarization vectors of two light beams are (a) parallel and (b) perpendicular. (c) The spectrum of $9f''$ produced via the intermediate state $3p^{1/2}_3 3d [3/2]_2$, denoted as $3d3$, when the polarization vectors of two light beams are parallel.

quite different from all the other spectra presented in this paper. The profile is a result of an admixture between a discrete Rydberg state and an ionization continuum [30–32]. The profile implies that the $9f''$ state produced via the $3d$ state has a greater admixture with the continuum than that of $3d'$. This may in part due to the fact that the $3p^{1/2}_3 3d [3/2]_2$ state has an ionic core same as the Ar$^+(3p^{3/2}_2)$ ion in the ground state so that it can be easily ionized by ir laser; this is evident by the high continuum background shown in Fig. 13(c). The line shapes will be further discussed later.

F. Quantum defect of the np$'[1/2]_0$ series

In accordance to the quantum defect theory [1,33], an ARS can be arranged into a Rydberg series by

$$E_m = I_p - R_{Ar}(n - \mu_n)^2,$$

where $E_m$ and $\mu_n$ are the resonance energy and quantum defect for the $n$ member of a Rydberg series, $I_p$ is the ionization potential (IP) of the series, and $R_{Ar}$ is the Rydberg constant for $^{40}$Ar. All the ARS in our study are converging to the second limit $^{40}$Ar$^+(3p^5p^{1/2}_1)+e^-$, for which the IP has been determined by many investigators [4,34–37]. Since our measurement covers to very high $n$ numbers, the $\mu_n$ values are very sensitive to the IP value used. The latest IP values are 128541.425(4) cm$^{-1}$ [36] and 128541.419(4) cm$^{-1}$ [37] that are determined from the fine structure splitting of $^{40}$Ar$^+(2p^{1/2}_2)P_{1/2}$ of 1431.5831 cm$^{-1}$ [38] and the first ionization potential energy of 127109.842 cm$^{-1}$ [36]. The average value of 128541.422 cm$^{-1}$ is used for the $\mu_n$ calculation. The $R_{Ar}$ value of 109735.809298 cm$^{-1}$ was used in this calculation which was determined from recent atomic data [37–41].

When the line shape was analyzed with the Beutler-Fano profile, we found that the fitted resonance energy $E_m$ is slightly different from the energy at the peak position $E_{pn}$. At high $n$, they are close together so that they are not distinguishable. For the lowest $n$ members we studied (i.e., $n=11$ for the np$'$ series and 9 for nf$'$), the difference of $\mu_n$ values calculated by the resonance and peak energies is on the order of 10$^{-3}$, which has no affect for the accuracy offered here. Therefore, we simply use the measured peak energy for quantum defect calculation.

The energies for peak positions and quantum defects for the np$'[1/2]_0$ series are listed in Table I. The peak energies are taken from the 5s$'$ intermediate state as shown in Fig. 3 for $n=11–29$, from 8s in Fig. 5 for $n=27–57$, and from 3d$'$ in Fig. 6 for $n=11–33$. For the overlapped $n$ region, the peak energy is averaged. The spectrum observed by Dunning and Stebbings [5,6] has unresolved structure of np$'$ states, but it may be dominated by the np$'[1/2]_0$ series. Their peak energies agree with our measurements within 1 cm$^{-1}$ for their highest members $n=24–26$, but there are generally lower for other members, for example, their values of 127269 or 127273 cm$^{-1}$ for $n=11$ is lower than our value of 127294.88 cm$^{-1}$ as listed in Table I.

The quantum defects are nearly constant for $n=9–30$, but they decrease about 2–5% for $n=31–47$, and then slightly increase for the higher $n$ members. The value averaged over all the $n=11–57$ members is 1.6111 (11), where the number in parenthesis is one standard deviation. Our result agrees very well with the value of 1.614(8) for the $n=11–20$ members determined by Koeckhoven et al. [7] with a four-photon excitation of Ar in the ground state. It is noted that Koeckhoven et al. [7] mistakenly assigned their spectrum to np$'[3/2]_2$, but it shall be np$'[1/2]_0$ as pointed out by Peters et al. [10]. Our value over the same $n=11–20$ range is 1.617(2). This good agreement confirms the assignment made by Peters et al. [10].

Using a single-electron Pauli-Fock approach, Petrov et al. [8] calculated the quantum defects for the 15p$'[1/2]_0$ and 20p$'[1/2]_0$ states to be 1.565 and 1.564, respectively, which are about 3% lower than our value of 1.615 for both members. Including core polarization and electron correlation effect in the Pauli-Fock approach, Petrov et al. [11] recalculated a quantum defect to be 1.599 for the $n=14$ member, which is only about 1% below our value. The agreement between experiment and calculation is very good.

G. Quantum defect of the np$'[3/2]_2$ series

The peak energies and quantum defects for the np$'[3/2]_2$ series are listed in Table II. The peak energies are taken from
the 5s' intermediate state shown in Fig. 3 for \( n = 11-16 \), from 7s' shown in Fig. 4 for \( n = 28-65 \), and from 8s shown in Fig. 5 for \( n = 28-42 \). The peak energy is an average value in the overlapped \( n \) region. The quantum defects are nearly constant up to \( n = 44 \), and then fluctuate within 7% around the overall average value of 1.686(13). The quantum defect for \( n = 13 \) and 14 measured by Peters et al. [10] with a single photon excitation from metastable \( \text{Ar}^* \) atom is 1.668(3), which is slightly lower than our value of 1.676(2) for the same \( n \) members. The theoretical value calculated by Pauli-Fock approach is 1.628 for \( n = 15 \). If core polarization and electron correlation effect is included, the value is 1.669.

### Table I. Peak positions \( E_p \) and quantum defects (QD) for the \( np' [1/2]_0 \) series.

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<th>( n )</th>
<th>( E_p ) (cm(^{-1}))</th>
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Average 1.611(11)

### Table II. Peak positions \( E_p \) and quantum defects (QD) for the \( np' [3/2]_2 \) series.

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<th>( E_p ) (cm(^{-1}))</th>
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Average 1.686(13)

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AUTOIONIZING RYDBERG SERIES

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for $n=14$; it is later revised to 1.667 [11]. This theoretical value is only lower than our value by 0.4%, a remarkable good agreement.

H. Quantum defects of the $np'$ ([$3/2$]) and ($[1/2]$) series

The peak energies and quantum defects for the $np'$[$3/2$] series are listed in Table III. The peak energies are taken from spectra observed with the polarization vectors of two light beams in orthogonal. The $7s'$, $8s'$, and $3d'$ intermediate states provide the data for $n=28–31$, $27–31$, and $11–18$, respectively. The peak energy is an average value for an overlapped $n$ member. The quantum defects are nearly constant for $n=11–18$, and they have a small fluctuation for large $n$ members. The overall averaged value is 1.688(10). Muhlpfordt and Even [37] observed an ARS, likely due to the quantum defects for these two states are almost identical too. This is consistent with the theoretical calculations that in considering the good agreement between theoretical calculation and our experimental observation, it is believed that the calculated value is reliable.

I. Quantum defect of the $nf'$ series

The observed $nf'$ series has a very long progression as shown in Table IV. The peak energies are taken from the $3d'$ spectrum in Fig. 6 for $n=9–26$, from $5d'$ in Fig. 7 for $n=26–74$, and from $6d$ in Fig. 8 for $n=28–70$. The peak energy is an average value in the overlapped $n$ region. The quantum defects are nearly constant for $n$ up to 56, and gradually increase for the high $n$ members. The overall averaged value is 0.016(5). Koeckhoven et al. [7] determined the value to be 0.010 (5) for $n=10–15$; Muhlpfordt and Even [42] gave a value of 0.072 (3) for $n=14–24$, compared to our value 0.005(3) averaged over $n=9–27$. Our result agrees better with the value from Koeckhoven et al. [7]. The theoretical value calculated by Pauli-Fock approach is 0.0005 for both $n=9$ and 20 [8–11]; and it is 0.00769 for $n=9$ if the core polarization and electron correlation effect is included in the Pauli-Fock approach [11]. Our value of 0.011 for $n=9$ agrees better with the latter calculation. Overall, our measurements again agree remarkable well with the theoretical calculations.

J. Autoionization width of the $np'[1/2]_0$ series

The ARS line shapes result from an admixture of discrete Rydberg states with ionization continua; they can be fitted by the Beutler-Fano profile [30–32]

$$I = I_0 + \sum_k I_k (q_k + \varepsilon_k)^2/(1 + \varepsilon_k^2)$$

(3)

$$\varepsilon_k = 2(E - E_{ik})/\Gamma_k,$$

(4)

where $I$ is the ion signal measured at energy $E$, $I_0$ is the background signal measured far away from the peak of a line, $I_k$, $q_k$, $E_{ik}$, and $\Gamma_k$ are the ion signal, $q$ parameter, resonance energy, and autoionization line width for a Rydberg state $k$, respectively.

As shown in Figs. 9–12, the $np'[1/2]_0$ series is well separated from nearby states so that it can be approximately treated as a single discrete state, and its shape can be fitted by the Beutler-Fano profile with $k=1$. Also, the observed width is much broader than the laser width; thus, the correction for the true linewidth with Eq. (1) is not needed. Instead of fitting the curve, a $q$ parameter can be determined from the ratio of the half-intensity ($\mu_{1/2}$) and quarter-intensity ($\mu_{1/4}$) widths of the shape measured relative to the continuum background. The $q$ parameter is determined by

$$q = [2(6a^2 - 1)/(1 - 5a^2)]^{1/2},$$

(5)

where $a = \mu_{1/2}/\mu_{1/4}$. The autoionization line width is determined by

$$\Gamma = q\mu_{1/2}/(q^2 + 2)^{1/2},$$

(6)

The resonance energy is determined from the energy at the peak $E_p$ by

TABLE III. Peak positions $E_p$ and quantum defects (QD) for the $np'$ [$3/2$] series.

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average 1.688(10)
The energy at peak positions, half-widths, quarter-widths, $q$ parameters, autoionization widths, reduced autoionization widths, and the differences of peak and resonance energies $E_r = E_p - \Gamma/2q$, are listed in Table V. The reduced autoionization width is given by

$$\Gamma_r = n^* \Gamma,$$

where $n^* = n - \mu_n$ is the effective principle quantum number. The data for the $11p' [1/2]_0$ state produced via $3d'[3/2]_1$ shown in Fig. 9 are also listed in Table V.

### Table IV. Peak positions $E_p$ and quantum defects (QD) for the $nf' [5/2]_2$ series.

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The average $q = 0.016(5)$.
The difference between the peak and resonance energies shown in Table V is 0.45 cm$^{-1}$ for $n=11$. The effective quantum defect calculated by this resonance energy of 127294.43 cm$^{-1}$ is 1.619, which is only slightly smaller than the value of 1.617 calculated by the peak energy as listed in Table I. This justifies that the quantum defect can be calculated with peak energy without introducing significant error. It is worth noting that the line shapes are fitted very well by the Beutler-Fano profile with the $q$ parameters determined by this method.

The reduced autoionization width is theoretically expected to be independent of the $n$ number for a Rydberg series [1]. However, the $\Gamma_r$ values in Table V show a large variation; especially, the value of 2549 cm$^{-1}$ for the $n=14$ member is much smaller than that of 4145 cm$^{-1}$ for $n=15$. The autoionization width results from the interaction between the discrete Rydberg state and ionization continuum [30]. The variation is mostly caused by the discrete state.

The averaged value of the reduced widths we measured at various $n$ is 3644(250) cm$^{-1}$; this is comparable to the values of 4050(600) and 3780(360) cm$^{-1}$ given by Koeckhoven et al. [7] and Petrov et al. [11], respectively. The theoretical values calculated by Pauli-Fock approach are 1783 cm$^{-1}$ for $n=9$ and 1924 cm$^{-1}$ for $n=20$ [8–11]; these values are much smaller than the experimental ones. When the core polarization and electron correlation effect is included in the Pauli-Fock approach, the calculated value is 3838 cm$^{-1}$ for $n=9$ [11], which agrees reasonably well with experimental data. These results indicate that the reduced width is a more sensitive way than the level energy to test theory.

**K. Autoionization widths of the np$^4$ ([1/2]$_1$ and [3/2]$_1$) series**

The np$^4$([1/2]$_1$) and [3/2]$_1$ series observed at orthogonal polarization vectors are overlapped together and mixed with the [3/2]$_1$ series as well. To get the widths and resonance energies, it requires fit the line profile with three channels in Eq. (3). The fitting procedure is cumbersome, and the obtained parameters are much less accurate. For the 11p$^4$[3/2]$_1$ state shown in Fig. 9, its intensity is weak and does not depend on the polarization angle so that it can be easily subtracted out from the spectra. Also, the 11p$^4$[3/2]$_2$ state is sharp and intense, it can be separated from the 11p$^4$[1/2]$_1$ state that is broad and weak. The autoionization widths determined from the 11p$^4$ ([1/2]$_1$) and [3/2]$_1$) states shown in Fig. 9 are about 3.6 and 0.4 cm$^{-1}$, respectively. This is consistent with the calculation by Petrov et al. [11] that the linewidth of the np$^4$[1/2]$_1$ state is about the same as that of np$^4$[1/2]$_2$, but it is about one order larger than that of np$^4$[3/2]$_1$.

**L. Linewidth of the np$^8$[5/2]$_2$ series**

As shown in Figs. 6–8, the np$^8$ [5/2]$_2$ series is well isolated from other states; thus, its linewidth can be determined by Eqs. (3)–(8) with the width ratios measured. The results for 9f$^2$ and 10f$^2$ produced via 3p$_{1/2}$ 3d$^3$ [3/2]$_1$ shown in Fig. 6 are listed in Table VI. It shows that the half-width is only about twice that of the laser width ~0.25 cm$^{-1}$; therefore, a correction on the observed width to get the true linewidth by Eq. (1) is needed. After the correction of laser width, the reduced autoionization widths are 318 and 324 cm$^{-1}$ for $n=9$ and 10, which are smaller than the uncorrected values of 395 and 456 cm$^{-1}$, respectively. Petrov et al. [11] calculated the reduced width for the $n=9$ state to be 185.7 cm$^{-1}$ using the Pauli-Fock approach, and decreases to 181.8 cm$^{-1}$ if configuration interaction and core polarization are included in calculation. Our value is higher than the calculated one by a factor of about 2; this difference is mainly caused by the laser resolution not good enough to measure the linewidth accurately.

The line shape produced via the intermediate state 3p$_{1/2}$ 3d$^3$ [3/2]$_1$ shown in Fig. 13(c) is another type of Beutler-Fano profile that can also be fitted by Eq. (3) with a $q$ parameter determined by

$$ q = ([I_p - I_r]/(I_c - I_m))^{1/2} $$

where $I_p$, $I_r$, and $I_m$ are the intensity at the peak, continuum, and minimum, respectively.

The autoionization width is determined by
\[ \Gamma = 0.5q(E_p - E_m)/(q^2 + 1), \]  

where \(E_p\) and \(E_m\) are the energies at the peak and minimum, respectively.

The \(q\) parameters, autoionization widths, and reduced autoionization widths for \(9f^\prime, 10f^\prime, 10f^\prime, \) and \(11f^\prime\) produced by the \(3d\{3/2\}\) intermediate state (also, see the spectrum published in our previous paper [16]) are listed in Table VI.

In this analysis, the \(q\) parameter is determined by relative intensities, and the autoionization width is determined by relative energies at the maximum and minimum intensities so that it is less affected by the laser width. The averaged \(\Gamma_r\) value for \(n=9-11\) as shown Table VI is 188 cm\(^{-1}\), which is in excellent agreement with the theoretical value of 181.8 cm\(^{-1}\) [11].

\[ \text{M. Photodissociation of the Ar}^{+}{\text{ion}} \]

Three broad bands are observed in the spectrum with peaks at 128391.57, 128424.97, and 128505.20 cm\(^{-1}\) in Fig. 4; two bands with peaks at 128445.63 and 128478.81 cm\(^{-1}\) in Fig. 5; and one weak band at 128438.50 cm\(^{-1}\) in Fig. 7. These bands are much broader than an atomic line. The \(^{40}\text{Ar}^+\) signals observed at these bands are likely produced from photodissociation of \(\text{Ar}^{+}\) and/or \(\text{Ar}^+\) dimer excited in Rydberg states. Radler and Berkowitz [24] have observed the \(\text{Ar}^+\) ion long ago when \(\text{Ar}\) atoms in the ground state were excited by synchrotron radiation to the intermediate states \(5s^\prime, 7s^\prime\), and 8s and the \(n\) number as well. For the intermediate states \(3d^\prime, 5d^\prime, \) and \(6d^\prime\), the intensity of the \(n^f\{5/2\}\) series is about two orders of magnitude stronger than those of \(np^\prime\). Such large variation is mostly related to the nature of the intermediate state. This result implies that this stepwise technique can be applied to study the nature of Rydberg states.

The spectrum produced by stepwise optical excitation is simple and easy to analyze so that each ARS is observed up to the \(n\) numbers much higher than published ones. Since a large number of a Rydberg series are observed, the quantum defects calculated will be more accurate. To extend the current study to other rare-gas atoms and possibly to molecules is of interest.

\[ \text{V. CONCLUDING REMARKS} \]

\text{Ar} atoms in the ground state are excited by synchrotron radiation to the intermediate states \(3p_{1/2}\{3d^\prime\{3/2\}\}, 5d^\prime\{3/2\}\), \(5s^\prime\{1/2\}, 7s^\prime\{1/2\}\), and \(3p_{3/2}\{6d\{1/2\}\}, 6d\{3/2\}\), and then excited by lasers to the autoionizing Rydberg series \(3p_{1/2}^m np^\prime\{1/2\}, \{1/2\}\), \(\{3/2\}\), \(\{3/2\}\), and \(nf^\prime\{5/2\}\). When the polarization vectors of two light beams are in parallel, one-photon excitation of the intermediate states \(5s^\prime, 7s^\prime, \) and 8s produces intense \(np^\prime\{1/2\}\) and \(3p^\prime\{3/2\}\) series but not the \(np^\prime\{1/2\}\) and \(3p^\prime\{3/2\}\) series. When the polarization vectors are in orthogonal, the \(np^\prime\{1/2\}\) series disappears and the \(np^\prime\{1/2\}\) and \(3p^\prime\{3/2\}\) series show up strongly. The spectral intensity depends on the angle between the polarization vectors of two light beams in accord with selection rules. This polarization effect is a powerful tool to identify Rydberg states. This technique can be extended to study the spectral properties of other rare gases and further to molecules.

The intensity distribution of the \(np^\prime\) series strongly depends on intermediate state. The intensity ratios of the two \(np^\prime\{1/2\}\) and \(3p^\prime\{3/2\}\) series vary dramatically with the intermediate states \(5s^\prime, 7s^\prime, \) and 8s and the \(n\) number as well. For the intermediate states \(3d^\prime, 5d^\prime, \) and \(6d^\prime,\) the intensity of the \(n^f\{5/2\}\) series is about two orders of magnitude stronger than those of \(np^\prime\). Such large variation is mostly related to the nature of the intermediate state. This result implies that this stepwise technique can be applied to study the nature of Rydberg states.

\[ \text{ACKNOWLEDGMENTS} \]

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