Two-photon Excitation: Investigation of Autoionizing Rydberg Series of Argon

Synchrotron radiation is used to excite the intermediate states of argon then excited by lasers to the autoionizing Rydberg series. For the intermediate states of 5s', 7s', and 8s of argon, the np' ($[1/2]_0$ and $[3/2]_2$) series are observed with high intensity but not the np' ($[1/2]_1$ and $[3/2]_1$) series when the polarization vectors of two light beams are in parallel; but when they are in orthogonal, the np' $[1/2]_0$ series disappears, the np' $[3/2]_2$ intensity remains, and the np' ($[1/2]_1$ and $[3/2]_1$) series show up strongly. The intensity distribution of the np' series strongly depends on the intermediate state of argon. The spectra of the np' series are assigned according to their intensity variation with the polarization vectors. The spectral line-shapes of autoionizing Rydberg states are analyzed with a Beutler-Fano profile. The quantum defect values and reduced autoionization linewidths of np' and nf' series are in excellent agreement with theoretical prediction. These improved optical data that include peak energy positions, linewidths, and polarization dependence are useful for testing further theoretical calculations.

Beamline

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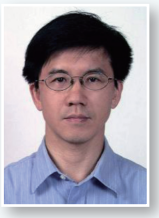

The odd-parity Rydberg series of Ar (*ns, ns', nd, and nd'*) have been extensively investigated, but the even-parity series of *np, np', nf, and nf'* are not well known. The odd-parity series can be reached by optical excitation of Ar in the ground state, $3p^6\ ^1S_0$, but the even-parity series are 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-parity autoionizing Rydberg series (EARS) 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.

Recently, Petrov *et al*. calculated the absorption cross sections to the four *14p'* ($[3/2]_2$, $[3/2]_1$, $[1/2]_1$, and $[1/2]_0$) states by optical-excitation from an initial state, $3p^5 4s$ *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. 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, the number of accessible states is limited; hence the EARS spectra are relatively simple and easy to analyze. We investigate the Rydberg series up to very high *n* members that are unreported.

The experiment was conducted by using the molecular beam two-photon excitation endstation which was comprised of two light sources and a vacuum chamber, containing a molecular beam source and a mass

spectrometer, as shown in Fig. 1. A noble gas beam was expanded through a nozzle (diameter 100 μm), skimmed into the interaction chamber and crossed with counter-propagating synchrotron radiation and laser beams in the ion-extraction region of a quadrupole mass filter (QMF) tuned at the mass of interested. The main chamber was typically operated at a pressure less than 3 x 10^{-7} Torr.

The SR was provided by the high-resolution monochromatic beamline (BL21B2) equipped with cylindrical gratings that select photons in the energy range of 6-120 eV with resolving power of $E/\Delta E > 10^5$. The slit width was set at 50 μm that gave a resolving power ~ 2×10^4 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 ~ 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 bi-refringent filter with a computer-controlled linear actuator, the Ti:Sapphire laser energy is tunable from 11690 – 13870 cm^{-1} (1.45-1.72eV); its highest output power is 750 mW and its spectral width is ~ 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 EARS, a mid-infrared OPO was implemented as the ionization source. 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 micro-stepping motor attached to a micrometer, controlled by a computer. The scanning range for the full width at half-maximum power at a single temperature and a crystal grating period was ~ 30 cm^{-1}. 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 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 to provide the reference wavelength.

The photoionization spectrum produced via first excitation with SR to the intermediate state $3p^5_{1/2}\,5s'\,[1/2]_1$ at 114975.02 cm^{-1} and then excited by a Ti:Sapphire laser at varied photon energies is shown in Fig. 2. ($3p^5_{1/2}\,7s'\,[1/2]_1$ at 123882.203 cm^{-1} and $3p^5_{3/2}\,8s\,[3/2]_1$ at 123935.87 cm^{-1}). In Fig. 2(a), the polarization vectors of two light beams are in parallel. The EARS positions for $3p^5_{1/2}$ ($np'\,[l/2]_0$, $np'\,[3/2]_2$ and $nf'\,[5/2]_2$) are indicated. The intensities of the $np'\,[3/2]_2$ state are weaker than those of $np'\,[l/2]_0$ for n =11, 12, and 14, but they are reversed for n = 13 and 15. The intensity of the nf' series is quite strong compared with those of the np'. When the angle, θ, between the polarization vectors of two light beams is rotated to 90°, the $np'\,[l/2]_0$ series disappears, but the np' ($[3/2]_1$ and $[1/2]_1$) series show up as shown in Fig. 2(b).

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

$$E_{rn} = I_p - R_{Ar}/(n - \mu_n)^2$$

where E_{rn} and μ_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, $^{40}Ar^+(3p^5\ ^2P_{1/2}) + e^-$, for which the IP has

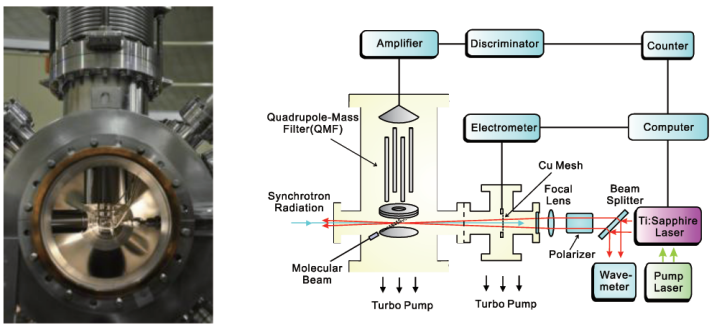

Fig. 1: Molecular beam two-photon excitation endstation. Left: Photograph of the interaction area in the system. Right: Schematic block diagram of the experimental setup.

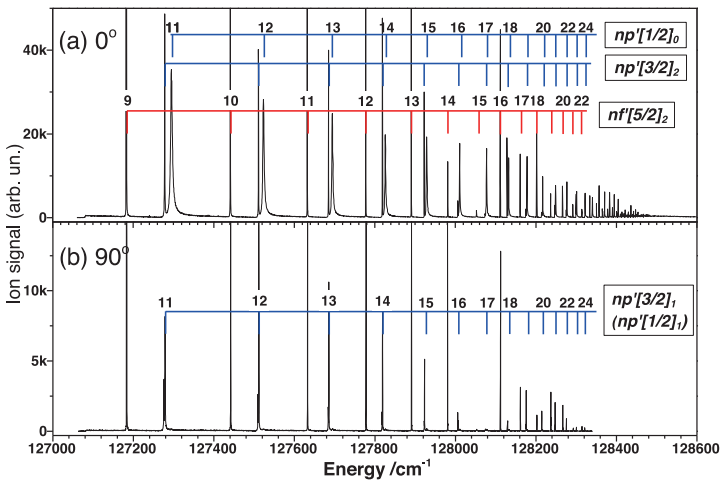

Fig. 2: Two-photon ionization spectra of Ar produced via the intermediate state $3p^5{}_{1/2}\,5s'\,[1/2]_1$. The abscissa denotes a wavenumber sum of the Ti:Sapphire laser and the intermediate state. The intensity is in arbitrary units. The polarization vectors of two light beams are in: (a) parallel, 0° and (b) perpendicular, 90°.

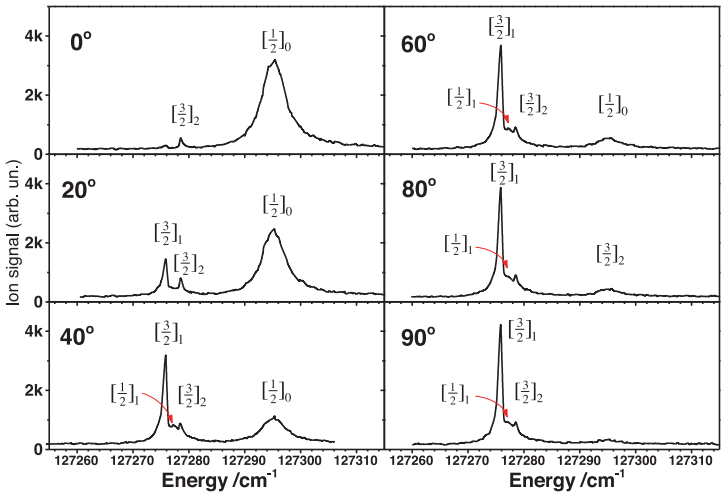

Fig. 3: Two-photon ionization spectra of Ar($3p^5{}_{1/2}\,11p'$) produced via intermediate state $3p^5{}_{1/2}\,3d'\,[3/2]_1$(115366.866 cm^{-1}). The abscissa denotes a wavenumber sum of the Ti:Sapphire laser and the intermediate state. The angles between the polarization vectors of two light beams vary from 0° to 90° as indicated.

been determined by many investigators. Since our measurement covers to very high *n* numbers, the μ_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} that are determined from the fine structure splitting of $^{40}Ar^+(^2P_{3/2} - {}^2P_{1/2})$ of 1431.5831 cm^{-1} and the first ionization potential energy of 127109.842 cm^{-1}. The average value of 128541.422 cm^{-1} is used for the μ_n calculation. The R_{Ar} value of 109735.809298 cm^{-1} was used in this calculation that was determined from recent atomic data. The quantum defects determined for the series, np' $[1/2]_0$ (n = 11–57), np' $[3/2]_2$ (n = 11–65), np' $[3/2]_1$ (n = 11–31), and nf' $[5/2]_2$ (n = 9–74), are 1.611±0.011, 1.683±0.013, 1.688±0.010, and 0.016±0.005, respectively.

The intensity of the *nf'* $[5/2]_2$ series is relatively intense compared with those of the *np'* ($[3/2]_1$ and $[1/2]_1$) series. The *np'* ($[3/2]_1$ and $[1/2]_1$) series are not optically-allowed at θ = 0°, but they become allowed at θ = 90°. Since the *nf'* $[5/2]_2$ 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. 2(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.

According to the j_cK-coupling principle that is generally applicable for noble gases and high *n* members, there are four states for an *np'* member, $3p^5{}_{1/2}\,np'$ ($[l/2]_0$, $[1/2]_1$, $[3/2]_1$, and $[3/2]_2$) accessible from the current studied intermediate states. When θ = 0°, the *np'* ($[l/2]_0$ 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. This selection rule is obeyed as shown in Fig. 3 at θ = 0°, 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 $M_J = \pm 1$ so that the *np'* $[l/2]_0$ state is not accessible.

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.* calculated that the line width of the *np'* $[1/2]_1$ state is about the same as that of $[1/2]_0$, but that of $[3/2]_1$ is about one order smaller. This confirms the assignment of the sharp peak at 12727.54 cm^{-1} shown in Fig. 3 to the *11p'* $[3/2]_1$ state and the broad band underneath to *11p'* $[1/2]_1$. It is conclusive that although the *np'* spectra vary in detail, the common structures are generally preserved for varied

intermediate states and polarization angles.

In summary, Ar atoms in the ground state are excited by synchrotron radiation to the intermediate states, $3p^5{}_{1/2}$ ($3d'$ $[3/2]_1$, $5d'$ $[3/2]_1$, $5s'$ $[1/2]_1$, $7s'$ $[1/2]_1$) and $3p^5{}_{3/2}$ ($6d$ $[1/2]_1$, $6d$ $[3/2]_1$, $8s$ $[3/2]_1$), and then excited by lasers to the autoionizing Rydberg series, $3p^5{}_{1/2}$ np' ($[1/2]_0$, $[1/2]_1$, $[3/2]_1$, $[3/2]_2$), and nf' $[5/2]_2$. When the polarization vectors of two light beams are in parallel, one-photon excitation of the intermediate states, $5s'$, $7s'$, and $8s$ produces intense np' ($[1/2]_0$ and $[3/2]_2$) series but not the np' ($[1/2]_1$ and $[3/2]_1$) series. When the polarization vectors are in orthogonal, the np' $[1/2]_0$ series disappears and the np' ($[1/2]_1$ and $[3/2]_1$) 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' series strongly depends on intermediate state. The intensity ratios of the two np' ($[1/2]_0$ and $[3/2]_2$) series vary dramatically with the intermediate states, $5s'$, $7s'$, and $8s$ and the n number as well. For the intermediate states, $3d'$, $5d'$, and $6d$ the intensity of the nf' $[5/2]_2$ series is about two orders of magnitude stronger than those of np'. 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 EARS 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.

Experimental Station

Molecular Beam Two-photon excitation end station

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