

Two-color Excitation Experiment

The different, partly complementary characteristics of lasers and synchrotron radiations (SR) provide new experimental possibilities and some particular advantages when the two light sources are used in combination. Studies of photoexcitation and photoionization in different subshells of many atoms and molecules have been performed during the past decade. In a "pump-probe" experimental scheme, the first photon is used to populate a particular, well defined excited state which is subsequently analyzed by the second photon. In this way it is possible to investigate various physical subjects, such as excited states which are not accessible by one-photon excitation due to dipole selection rules; processes related to photo-induced molecular dissociation, consequences of a change in the electronic configuration for the photoionization of a particular subshell; probing even-parity autoionizing states or effects related to aligned or oriented species Fig. 1.

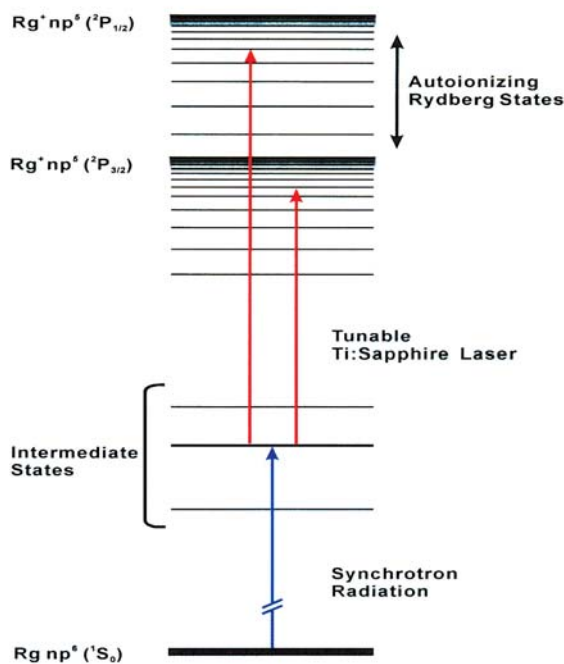


Fig. 1: Energy diagram indicating the two-photon excitation pathway used in atomic rare gases.

In the present work, we report improved spectra of the even-parity autoionizing Rydberg series of Ar and Xe in the region between $^2P_{3/2}$ and $^2P_{1/2}$ ionic thresholds by means of double-resonant two-photon excitation using SR and a Ti:Sapphire (Ti:S) laser.

Experiment

For these purposes, a mode-locked Ti:S laser system is modified to operate synchronously with the storage ring of NSRRC. The synchronization scheme is shown in block form in Fig. 2.

Since it is passively mode-locked the laser repetition rate is determined by the cavity length. By carefully controlling the cavity length, it can be frequency locked to a reference oscillator. We extract the revolution frequency of storage ring 2.5 MHz as base frequency, and multiple it by a factor of 32 to get 80 MHz stable output to drive the mode locker. Rough cavity length adjustment of the Ti:S laser to the storage ring master frequency is provided by a stepper motor attached to the high reflectivity end mirror. Fine adjustment of the cavity length is facilitated by a fold mirror (M_4) in the cavity mounted on a piezoelectric translator

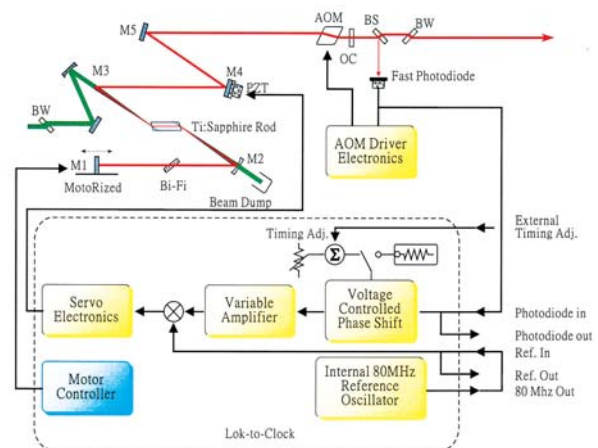


Fig. 2: Schematic diagram of the clock-locking system for the Ti:S laser.

(PZT) which is driven in response to the compensator signal generated by Lok-to-clock, a phase lock loop device for Ti:S laser system. After this step, it is necessary to tune the phase shift between the two light sources. Two stages are done to manipulate the time delay, first tune the EG&G 425A ns delay module to adjust the phase shift in ns's region. Fine control of the phase is adjusted using an electronic phase shifter inside the Lok-to-clock module, which has a range of 2 ns.

In this way, the laser pulse can match the third generation synchrotron radiation pulse in 20 MHz maximum at 8-bunch operational mode with tens picosecond time resolution in pump-probe operation Fig. 3.

The experimental apparatus consists of a chamber, containing a molecular beam and a photoionization mass spectrometer, and two photon sources. In order to obtain greater ion signals, we replaced the skimmed molecular beam source with an effusive beam source, using a small capillary with an inside diameter of less than 50 μm . Argon or Xenon ($> 99.999\%$, < 10 Torr) was expanded through the capillary and crossed by the synchrotron radiation and the laser emission in the ion-extraction region of a quadrupole mass spectrometer (QMS), as shown in Fig. 4. The main chamber was typically operated under a pressure less than 3×10^{-7} Torr. The synchrotron radiations, with a flux of 5×10^{15} photon s^{-1} (3% BW at 15eV) come from an undulator beamline of a 9 cm

magnetic period and 47 effective periods.

The high resolution monochromatic beamline, BL21B2, equipped with a set of cylindrical gratings, provides photons with energies in the range of 5-120 eV with a maximal resolving power $E/\Delta E$ of $> 10^5$. The slit widths were set at 50 μm , corresponding to a resolving power of $\sim 2 \times 10^4$ at 14 eV. The near infrared radiations from a Ti:S laser counter-propagate with the synchrotron radiations and are mildly focused to a diameter ~ 0.5 mm at the ion-extraction region of the QMS to match the beam spot of the synchrotron radiation. The wavelength of the laser may be tuned from 720 to 860 nm (corresponding to photon energies of 1.72-1.45 eV) by rotating a birefringent filter using a computer controlled linear actuator. The maximal output power is 750 mW and the spectral width is ~ 1 cm^{-1} . The laser output is linearly polarized with an extinction ratio of greater than 300. With a half-wave Fresnel rhomb, the polarization of the laser light may be rotated.

To reduce undesired ionization produced with higher order light, a gas filter was installed near the exit of the monochromator. With 3 Torr of helium in the gas cell, photons with energies greater than 24.5 eV were efficiently suppressed to less than 0.01%. To reject the ions produced from background gases, the QMS was set at $m/e=40$ and 132 for Ar and Xe atoms, respectively. These modifications enabled us to record excitation spectra with an improved signal-to-noise ratio and with little interference.

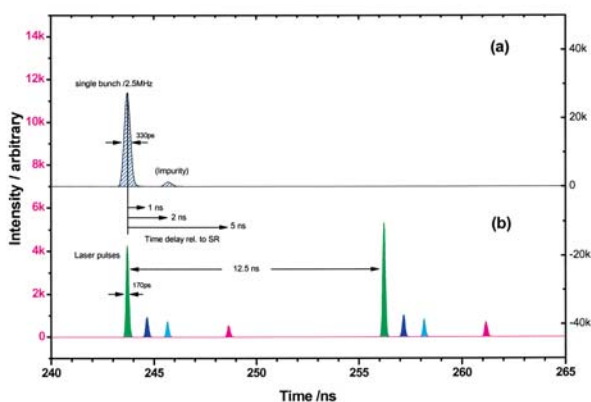


Fig. 3: Two-color experiment pump-probe scheme: Time correlation between the S.R. and mode-locked Ti:S laser pulses. (a) Synchrotron radiation pulse in single bunch operational mode. (b) Timing of probe laser pulses were adjusted relative to the S.R..

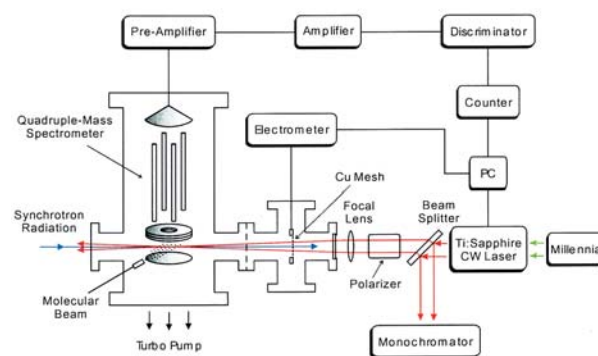


Fig. 4: Schematic experimental setup for the measurement of the two-photon ionization of rare gases.

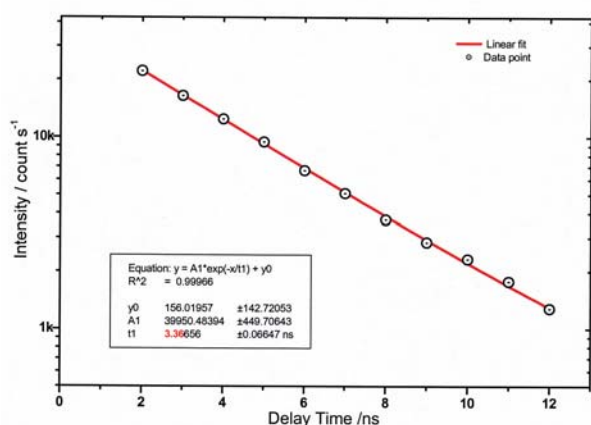


Fig. 5: Two-photon ionization signal of Xenon as a function of the laser and synchrotron radiation pulses.

Results and discussion

As an example we have measured the resonant two-photon ionization of Xe atoms, in first step the Xe atoms are excited by the S.R. pulse to the $\text{Xe}^*5p^5(^2P_{1/2})5d'[3/2]_1$ resonance at $h\nu=11.607\text{eV}$. Only if the second photon of the laser pulse arrives within the lifetime of the $\text{Xe}^*5p^5(^2P_{1/2})5d'[3/2]_1$ excited state, an ionization signal due to the two-photon process is detectable. The recorded electron signal as a function of the delay between the laser and the S.R. pulse is depicted on Fig. 5. A total accumulation time of 10s for each point was applied in order to extract the signal from a single-bunch operation of synchrotron radiation.

For the resonance two-photon ionization at autoionization region, $\text{Xe}^*5p^5(^2P_{1/2})5d'[3/2]_1$ Rydberg state was populated by S.R. and was used as an intermediate state to probe the even-parity Rydberg series lying between $^2P_{3/2}$ and $2P_{1/2}$ ionic thresholds by further excitation with the tunable Ti:Sapphire laser in the spectral range of 841.72–721.51 nm. The resulting spectrum is shown in Fig. 6 representing the signal of the two-photon ionization as the total energy of two photons. The observation of the forbidden transitions, nf' and np' , between the core configurations indicates a strong configuration interaction. These series were reported by Meyer et al. based on results from the SuperACO storage ring.

By tuning the energy of SR to 14.153 and 14.304 eV (corresponding to 114,147.7 and

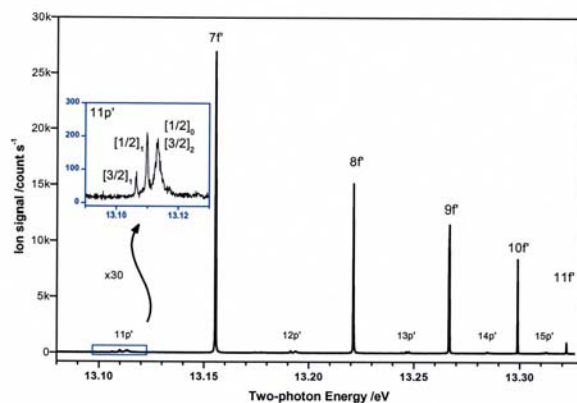


Fig. 6: Double-resonance photoionization spectra of Xe. Two-photon ionization of the np' and nf' resonances via $\text{Xe}^*5p^5(^2P_{1/2})5d'[3/2]_1$. Inset shows an enlarged region of np' series with a vertical magnification of 30.

$115,366.8\text{ cm}^{-1}$), the Ar $3p^5(^2P_{3/2})3d [3/2]_1$ and $3p^5(^2P_{1/2})3d' [3/2]_1$ autoionization resonances, respectively, can be excited within the wavelength region of the tunable cw laser.

Figure 7 shows the photoionization spectra as a function of the total energy of two photons. Trace (a) is a spectrum recorded when the Ar intermediate state $3p^5(^2P_{3/2})3d [3/2]_1$ is excited, with polarizations of both excitation beams parallel; the intensity of the ion signal increases dramatically when the total photon energy exceeds $127,078\text{ cm}^{-1}$ (15.756 eV), $\sim 32\text{ cm}^{-1}$ below the threshold to form $\text{Ar}^+ (^2P_{3/2})$. Similar thresholds for appearance of ion signals were previously reported by Radler and Berkowitz, and Koeckhoven *et al.* The energy difference between the ionization threshold and the threshold for ion signal may be accounted for by the electric field effect in the ion-extraction area of the QMS and the collision-induced ionization. The spectrum exhibits a series of lines with Fano-type asymmetric band shapes on top of an intense continuous background. This progression can be readily identified as the $3p^5nf' [5/2]_2$ based on a previous report using a four-photon excitation method. By applying the literature value for the ionization potential of Ar to form $\text{Ar}^+ (2P_{1/2})$, $128,541.2\text{ cm}^{-1}$, the quantum defect of this series is derived to be 0.01 ± 0.01 for $n=9-13$, consistent with a value of 0.010 ± 0.005 reported previously for $n = 10-15$.

Trace (b) of Fig. 7 shows the photoionization spectrum recorded when the intermediate state

$3p^5(^2P_{1/2})3d' [3/2]_1$ is excited with the SR at 14.304 eV (115366.8 cm^{-1}) and the Ti:Sapphire laser with a parallel polarization was tuned. The spectrum consists of a weak continuous background and two series of lines, both converging to the $\text{Ar}^+ (^2P_{1/2})$ ionic threshold. The intense series is identical to that shown in Trace (a) for the $3p^5nf' [5/2]_2$ series, except that line shapes of this series are nearly symmetric.

The weak series, with intensities about 1% of those of the $3p^5nf' [5/2]_2$ series, exhibits broader line widths with a full width at half maximum (FWHM) of $6 \pm 1 \text{ cm}^{-1}$ for the first two members of the series. Upon careful examination, we found that each line of this series had a weaker component at the lower energy side. Relative intensities of these two components reverse as a function of the laser light varies from parallel to perpendicular relative to the polarization of S.R., further studies are undergoing to probe these fascinating phenomena.

In summary, we developed a Ti:S laser coupling with the high-resolution synchrotron radiations to perform two-photon excitation of Ar and Xe to their even-parity autoionizing states $3p^5np' [3/2]_2$, $3p^5np' [1/2]_0$, and $3p^5nf' [5/2]_2$, lying between the $^2P_{3/2}$ and $^2P_{1/2}$ ionic thresholds. The series $3p^5np' [3/2]_2$ and $3p^5np' [1/2]_0$ are resolved for the first time. Excellent signal-to-noise ratios in the two-photon ionization spectra

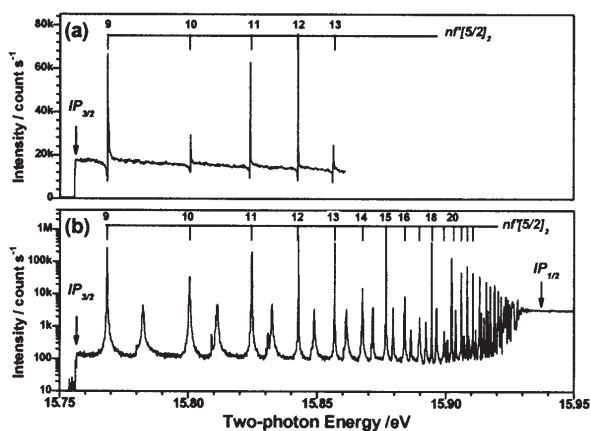


Fig. 7: Double-resonance photoionization spectra of Ar. Two-photon ionization of the np' and nf' resonances via $\text{Ar}^*3p^5(^2P_{3/2})3d[3/2]_1$ (a) and $\text{Ar}^*3p^5(^2P_{1/2})3d'[3/2]_1$ (b) Rydberg states.

demonstrate that we have succeeded in the application of a tunable laser combined with the S.R. of the NSRRC storage ring. The resolution and precision of these experiments are mainly limited by the laser, hence they might be further improved if a frequency-stabilized ring dye laser is employed.

Beamline:

21B2 U9/High Resolution Spectroscopy beamline

Experimental Stations:

PIMS end station

Laser-SR two-color experiment project

Authors:

Y. Y. Lee, K.-T. Hsu, and K.-K. Lin

National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Publications:

- Y.-Y. Lee, K.-T. Hsu, and S.-H. Lee, SRRC Newsletter **43**, 9 (1999). (in Chinese)
- Y.-F. Song, P.-C. Tseng, L.-R. Huang, S.-C. Chung, T.-E. Dann, C.-T. Chen, and K.-L. Tseng, Nucl. Instrum. Methods A **467**, 496 (2001).
- J.-C. Lee, SRRC Newsletter **50**, 15 (2002). (in Chinese)
- Y.-Y. Lee, T.-Y. Dung, and R.-M. Hsieh, Chem. Phys. Lett., (submitted).
- Y.-Y. Lee, T.-Y. Dung, R.-M. Hsieh, J.-Y. Yu, Y.-F. Song, K.-T. Hsu, AIP Conf. Proceedings, San Francisco, (submitted).

Contact e-mail:

yylee@srcc.gov.tw