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Resonance Ionization Spectroscopy of Argon, Krypton, and Xenon Using Vacuum Ultraviolet Light

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Resonance Ionization Spectroscopy of Argon, Krypton, and Xenon Using Vacuum Ultraviolet Light

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Abstract. Resonant, single-photon excitation of ground state inert gases requires light in the vacuum ultraviolet spectral region. This paper discusses methods for generating this light. Efficient schemes for ionizing argon, krypton, and xenon using resonant, stepwise single-photon excitation are presented.

1. Introduction

A prerequisite for the use of the resonance ionization spectroscopy (RIS) detection technique is a method for resonantly ionizing with high efficiency the species of interest. The application of this technique to heavy inert gas detection requires a means of efficiently exciting atomic transitions that lie in the vacuum ultraviolet (VUV) region of the spectrum.

A two-photon excitation scheme has been experimentally demonstrated in both xenon and krypton and has been evaluated theoretically (Chen et al 1980, Bokor et al 1980, Payne et al 1981). The krypton excitation scheme, however, made use of the fact that a two-photon allowed level lies within the narrow tuning range of the ArF laser near 193.0 nm. This accidental coincidence makes it impossible for this method to be extended to argon. In addition, tight focusing and high peak powers over the Doppler linewidth are required for efficient ionization using two-photon excitation. These complicate the background problem due to off-resonant multiphoton ionization of impurities. As a result, a detection system based on the one-photon excitation of the inert gases would be preferable for many applications. This paper describes efficient schemes for the one-photon excitation and subsequent ionization of krypton, xenon, and argon.

2. Resonance Ionization of Krypton

Figure 1 shows a two-photon resonant, three-photon ionization scheme that has been used to resonantly ionize krypton (Kramer et al 1983, 1984a; Chen et al 1984a). To excite the 5s′ transition shown, VUV radiation at the vacuum wavelength of 116.49 nm is required. The s′ excitation is a strongly allowed transition which has a measured (Matthias et al 1977) oscillator strength of ~0.2. A 0.2-cm^{-1} bandwidth would be broad enough to excite over the Doppler, hyperfine and isotope manifold of krypton and would require a power density of only ~700 W/cm^2 in order to saturate the transition (Payne and Hurst 1984, Jackson 1980). This is very much smaller than the 10^{10} W/cm^2 needed to saturate a nearby two-photon allowed transition (Bokor et al 1980). Earlier work (Yiu et al 1982, Hilbig and Wallenstein 1982) with four-wave mixing in xenon indicated that this could be a promising method to generate the VUV radiation for the initial one-photon excitation although the required power, bandwidth, and wavelength had not been simultaneously produced.

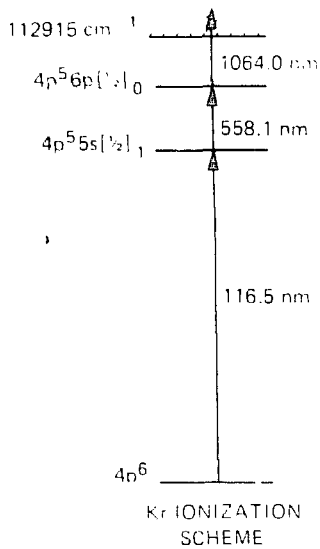
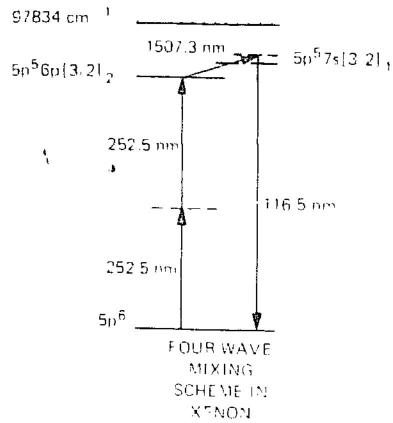


Fig. 1 Krypton resonance ionization sectroscopy scheme

Although it is possible to directly ionize the krypton 5s' excited state, the photoionization cross section at threshold is only 2×10^{-19} cm^2, and it rapidly decreases towards a Cooper minimum in the region of 200.0 nm (Duzy and Hyman 1980). However, by using another laser tuned to 558.1 nm, krypton in the $4p^5 5s'[1/2]_1$ state can be excited to the $4p^5 6p[1/2]_0$ state. This is a strongly allowed transition that can easily be saturated with the output of a small dye laser. The 6p state then can be efficiently ionized using the 1.06-μm fundamental of a Nd:YAG laser. Since the photoionization cross section from the p state is $\sim 1.5 \times 10^{-17}$ cm^2, a modest fluence of 0.03 J/cm^2 will saturate the ionization step (Chang and Kim 1982).

Figure 2 shows the relevant energy levels in the xenon four-wave mixing scheme, and Fig. 3 depicts a simplified diagram of the experimental apparatus used for the generation of the radiations at the wavelengths needed for resonance ionization of krypton according to the scheme shown in Fig. 1. The 200-mJ/pulse, second harmonic output of a 10-Hz, Q-switched Nd:YAG laser (Quanta-Ray DCR-1A) was split equally into two beams and used to pump dye lasers 2 and 3. The wavelength, at 252.5 nm, which was tuned to excite the $5p^5 6p[3/2]_2$ two-photon allowed transition in xenon, was generated by mixing the doubled output of dye laser 3 (Quanta-Ray PDL) with the residual 1.06 μm pump laser output. This required dye laser 3 to be tuned to 661.9 nm. Dye laser 2 (Quanta-Ray PDL) pumped a high pressure hydrogen Raman cell whose second Stokes shifted output produced radiation at 1.5073 μm when dye laser 2 was tuned to 669.0 nm. Both dye lasers were used with DCM dye (Exciton Corp.). In order to shift the tuning curve of the dye to the spectral region needed, dimethyl sulfoxide was used as a solvent in the oscillator stages of both tunable dye lasers (Chen and Kramer 1984).

The linearly polarized beams at 252.5 nm and near 1.5 μm were separated from their respective generating wavelengths by using Pellin-Broca prisms, which for simplicity are not shown in Fig. 3. To optimize the light transmission through the prisms, polarization rotators were used. Both lasers 2 and 3 produced visible light with a bandwidth of 0.3 cm^{-1}. The Nd:YAG fundamental output had a bandwidth of ~1 cm^{-1}. Under these conditions the calculated VUV bandwidth would be ~1.5 cm^{-1}. The light pulses at 252.5 nm and near 1.5 μm, both of which contained ~0.2 mJ were focused with separate lenses and made coaxial by use of a dichroic beam



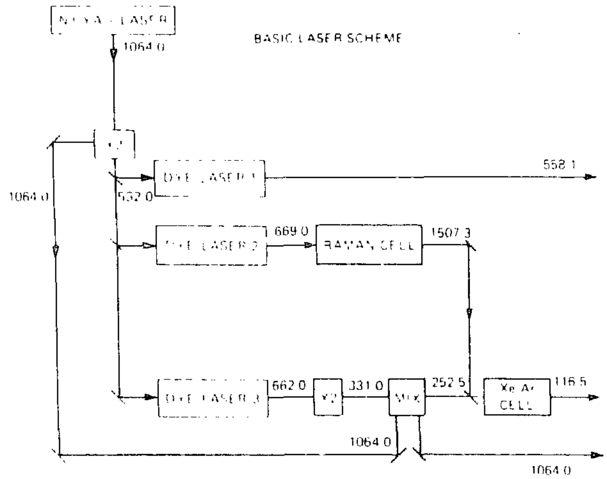


Fig. 2. Four-wave mixing scheme in xenon

Fig. 3 Basic laser schematic. The three beams at 558.1, 116.5, and 1064 nm were focused to overlap at the ion entrance aperture of the mass spectrometer. Wavelengths are shown in nanometers.

splitter before entering the xenon VUV generation cell. The effective lens focal lengths of ~42 cm and positions as well as the beam diameters were chosen so that the focal points and confocal parameters for both wavelengths would be approximately the same (Bjorklund 1975). About 10% of the second harmonic output of the Nd:YAG laser pumped a small dye laser 1 (NRG Corp.) in order to generate 2 mJ/pulse of 558.1-nm radiation as shown in Fig. 3. Approximately 70 mJ of the Nd:YAG laser fundamental radiation was used to complete the resonance ionization spectroscopy (RIS) process of Fig. 1.

Since Xe is negatively dispersive in the region from 113.5 to 117.0 nm, the VUV output can be increased by phase matching with a gas such as argon which is positively dispersive in the region of interest (Bjorklund 1975, Mahon et al 1979). Phase matching over the range from 115.7 to 116.9 nm required ratios of argon to xenon pressure from ~5 to 180, which is consistent with known refractive indices (Kramer et al 1984b, 1984c).

In particular, at 116.49 nm, which is the krypton resonance wavelength, the required argon-xenon ratio was 9.2. A typical VUV tuning curve with this gas mixture is shown in Fig. 4. The VUV light is tuned by changing the wavelength of dye laser 2. In this wavelength region, the VUV tended to saturate at ~0.3 μJ at pressures above ~60 Torr of xenon. This gives a photon conversion efficiency of ~0.1%. A tendency for the VUV to saturate with increasing xenon pressure occurred throughout the tuning range studied. This might be related to xenon ionization in the cell. However, no saturation effects were seen as the power of the two input wavelengths in the four-wave mixing process was varied. In general, the amplitude of the output from 115.7 to 116.9 nm was always above 0.2 μJ and peaked at 0.7 μJ in the region near 115.8 nm. This is the highest reported pulse energy that has been produced in this wavelength region.

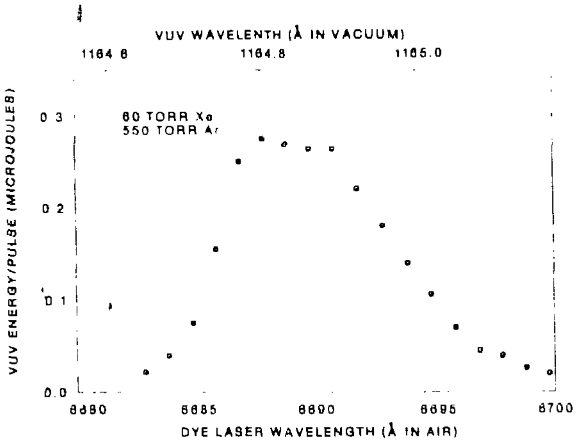


Fig. 4 VUV tuning curve

To generate light at the strong krypton resonance line, the amount of krypton impurity in the xenon and argon gas must be kept to a minimum. It was found experimentally that when gases containing less than 2 ppm of krypton (Spectra Gas Corp.) were used, the krypton ionization signal increased by a factor of 3 over that obtained when gases containing about 20 ppm of krypton (Matheson Corp.) were used.

A LiF exit window was used on the xenon-argon VUV generation cell in order to maximize the transmission at 116.5 nm. The flange holding this window could then be directly attached to a krypton detection chamber. A LiF lens could be used to focus the VUV light, but in many applications this may not be necessary. In our system the unfocused VUV light had a diameter of ~1 mm at a distance of 15 cm past the focal point in the VUV generation cell (Bjorklund 1975). The ionization region of a quadrupole mass spectrometer in the krypton detection chamber was positioned at this spot. At this point the VUV beam diameter was well matched to the 1 mm acceptance aperture of the mass spectrometer.

After leaving the krypton detection cell through a second LiF window, the VUV light entered a two-stage VUV detection chamber. The first stage was filled with up to 600 Torr of a mixture of 1% nitric oxide (NO) in argon to serve as a VUV beam attenuator. The second stage, which was separated by another LiF window from the first stage, was an ionization chamber. The electrode and guard ring geometry was such that only ionization that occurred in the center 1.5 cm of the 15-cm long, second-stage cell was detected using a charge sensitive preamplifier. Since the absolute photoionization cross section of NO in this wavelength region is known (Watanabe et al 1967), filling the second stage with known amounts of a 1% NO in argon mixture allowed an absolute measurement of the amount of VUV light that was produced. A gas mixture rather than pure NO was used to simplify pressure measurements and to provide suitable operating conditions for the ionization chamber. All the LiF windows (Harshaw Corp.) used in the experiment were 3 mm thick and had measured transmissions of ~40%.

As already indicated, in the actual krypton detection region the VUV light diameter was ~1 mm. The two other wavelengths, 558.1 nm and 1.06 μm, shown in Fig. 1, which were necessary for efficiency krypton ionization, were focused to 3-mm beam diameters and were made coaxial with the generated VUV beam. It was found experimentally that the 5s' to 6p transition and the final photoionization step were saturated. With a 2-mJ/pulse beam at 558.1 nm and a 70-mJ/pulse beam at 1.06 μm, this is constant with calculated cross sections for these transitions (Chang and Kim 1982). The VUV excitation step showed virtually no evidence of saturation, and so it was the rate limiting step. Calculations indicate that the 116.5-nm pulse described in this paper should be within a factor of 10 of complete (>95%) saturation of the initial excitation step in krypton (Matthias et al 1977, Payne and Hurst 1984). Actual experiments demonstrated that with this system, krypton atoms within a volume of $\sim 2 \times 10^{-3}$ cm^3 could be ionized with at least 10% efficiency (Kramer et al 1983). Optimization of the system using more sophisticated optical components and krypton ion collection electrodes should result in an ionization efficiency of close to 100% over a volume of at least 10^{-2} cm^3.

3. Resonance Ionization of Argon

The lowest energy level in argon that can be reached by an allowed one-photon excitation from the ground state is the $3p^54s[3/2]_1$ state. One-photon excitation of this state requires a photon with a wavelength of 106.67 nm. This is close to the transmission cutoff of a LiF window. However, it is still a long enough wavelength that a 2 mm thick LiF window will have a transmission of ~25%. As was the case in krypton, the photoionization cross section from this argon s state is rather small. Therefore, as shown in Fig. 5, light at a wavelength of 365.9 nm can be used to promote argon in the 4s excited state to a higher lying $3p^56p[1/2]_1$ state. This 6p state is close enough to the argon ionization limit that it can be efficiently ionized using the fundamental output of a Nd:YAG laser. The required pulse energies for each of the three wavelengths depicted in Fig. 5 are comparable to the corresponding requirements in the previous krypton ionization example (Matthias et al 1977, Duzy and Hyman 1980).

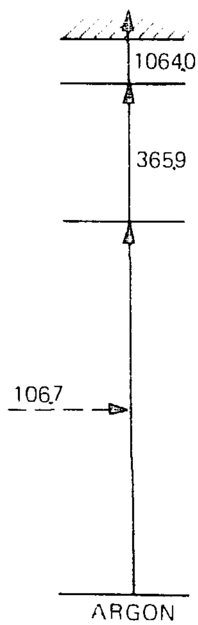


Fig. 5 Argon resonance ionization scheme

The generation of the 106.7 nm light can be accomplished using a two-photon resonant, four-wave mixing process in xenon. The method, as depicted in Fig. 6, would be very similar to that used to generate the 116.5 nm light for the ionization of krypton. The efficiency for generation of the 106.7 nm light should be about the same as that for 116.5 nm light. Vacuum ultraviolet light at 106.7 nm lies just above the $5p^55d[3/2]_1$ state in xenon. Therefore, xenon is negatively dispersive at this wavelength and it can be phase matched (Mahon et al 1979, Zapka et al 1981). Krypton would be a suitable phase-matching gas since it is positively dispersive at this VUV wavelength (Mahon et al 1979).

A practical laser system for argon ionization is shown in Fig. 7. It is very similar in design to the system previously described for the detection of krypton, and it should have a similar capability. There are two major changes. The first is that the output of dye laser 1 at 557.7 nm would have to be mixed with a portion of the Nd:YAG fundamental at 1.06 μ in order to generate the required wavelength of 365.9 nm. The second change is simply to use the dye pyridine 1 in dye laser 1.

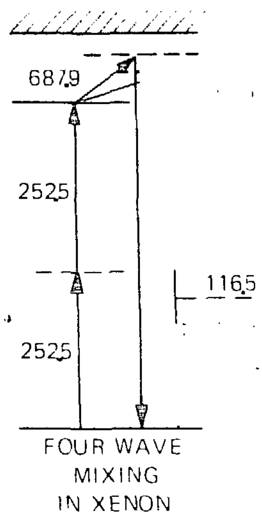


Fig. 6 Four-wave mixing scheme in Xe used for Ar detection

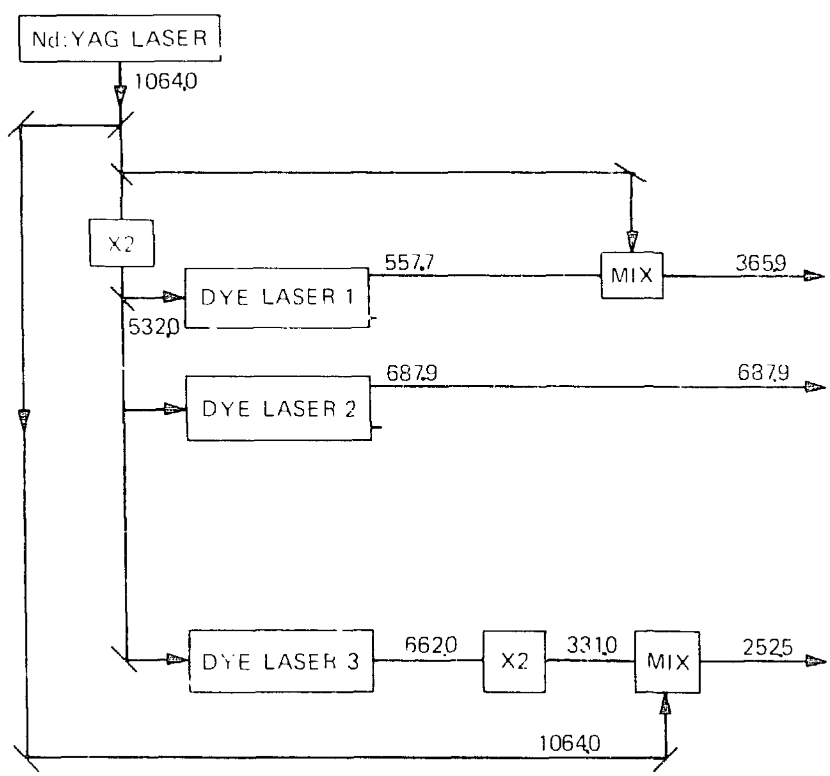


Fig. 7 Basic laser schematic for argon detection

4. Resonance Ionization of Xenon

Figure 8 shows an efficient scheme for the ionization of xenon. The $5p^6$ ground state of xenon is excited to the $5p^5 5d[1/2]_1$ level by a photon of wavelength 125.02 nm. The ionization cross section from the 5d state should be large enough that about 10 mJ of second harmonic light at 532 nm from a Nd:YAG laser should be enough to saturate the transition over a 1-mm beam diameter.

Previous work has indicated that the required 125.02-nm light can be easily generated by using the two-photon resonant, four-wave mixing process in mercury shown in Fig. 8 (Tomkins and Mahon 1981). More than 20 μJ/pulse at 125.02 nm was produced, using the system shown in Fig. 9 (Mahon and Tomkins 1982). In that experiment the mercury pressure was about 1.4 Torr, and the mercury cell also contained 15 Torr of helium buffer gas. The residual 312.85-nm light used to generate the VUV wavelength can also ionize xenon from the 5d state, and in many cases it may not be necessary to have a separate 532-nm beam for this purpose.

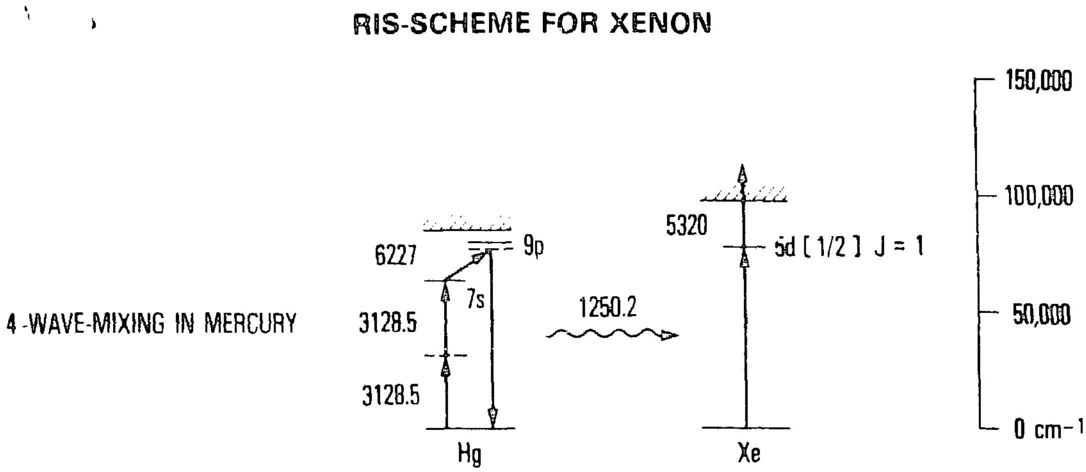


Fig. 8 Xenon resonance ionization scheme and the four-wave mixing scheme in Hg used for Xe detection (wavelengths in Angstroms)

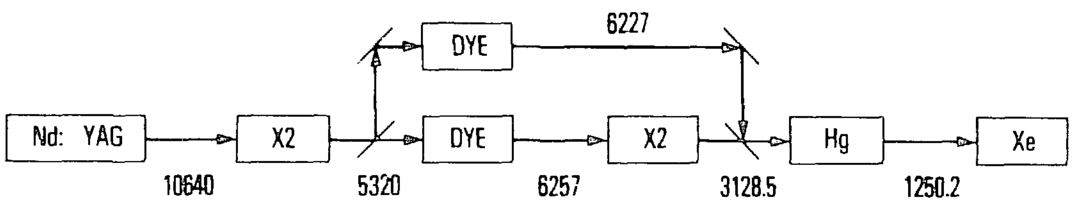


Fig. 9 Basic laser schematic for Xe detection

This method for xenon detection is quite practical. With the same lasers, it should have about 10 times the detection efficiency of the krypton and argon detection method.

5. Conclusions

Practical methods for the resonance ionization of krypton, argon, and xenon have been proposed. In the case of krypton, actual experiments showed that a krypton atom in a 2 x 10^{-3} cm^3 volume could be detected with a 10% probability, using a single detection laser pulse. Similar experiments with argon and xenon should produce even better results.

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