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Absolute photoionization cross sections with ultra-high energy resolution for Ar, Kr, Xe and N_2 in inner-shell ionization regions

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Abstract

The high-resolution absolute photoionization cross sections for Ar, Kr, Xe and N_2 in the inner-shell ionization region have been measured using a multi-electrode ion chamber and monochromatized synchrotron radiation. The energy ranges of the incident photons for the target gases were as follows: Ar: 242–252 eV (2p Rydberg excitation), Kr: 1650–1770 eV (near the 2p ionization thresholds), Xe: 665–720 eV (near the 3d ionization thresholds) and 880–1010 eV (near the 3p ionization thresholds), N_2: 400–425 eV (N 1s excitation and ionization). It is the first time to measure the absolute ionization cross sections of Ar, Kr, Xe and N_2 over the present energy ranges with the energy resolution of over 10,000. The natural lifetime widths of $2p_{3/2}^{-1}4s$, $2p_{3/2}^{-1}3d$, $2p_{3/2}^{-1}4d$ and $2p_{1/2}^{-1}4s$ resonances for Ar, $3d_{5/2}^{-1}6p$ resonance for Xe, and $1s^{-1}\pi_g^*(v'=0)$ resonance for N_2 have been obtained based on the cross sections determined. The ionization energies into the Ar^+ ($2p_{3/2}^{-1}$), Ar^+ ($2p_{1/2}^{-1}$) and Xe^+ ($3d_{5/2}^{-1}$) ionic states are also determined using the Rydberg formula.

Keywords: Photoionization cross section; Argon; Krypton; Xenon; Nitrogen; Inner-shell electron

1. Introduction

Photoabsorption spectra and photoionization spectra are often used for monochromator calibration or derivation of natural lifetime widths of the corresponding hole states. Generally speaking, the natural lifetime widths and transition energies based on the absolute cross sections are more reliable than those based on ion yield spectra because the ion yields are often influenced by the saturation effect of measurements, i.e. the ion currents measured with an ion detector such as micro-channel plates are not proportional to the cross section due to dead time or pile-up for the high count rate. Furthermore the absolute cross sections of the rare gas atoms in the soft X-ray region are utilized for the measurement of absolute photon intensities [1,2]. For these reasons, the absorption spectra are required to be converted to photoabsorption cross sections on absolute scale for both the energy values and the cross section values, and are desirable to be measured with as high resolution as possible. A number of measurements on photoabsorption cross sections have been performed using various techniques and different light sources by several research groups [3–24]. One of the serious problems in determining the absolute cross section values is the mixing of impurity photons into the incident beam, for example, stray light and higher order radiation. Yang and Kirz [15] examined the dependence of the signals on the density of the sample gas in a gas cell and determined the photoabsorption cross section for Ar for the first-order photon. Samson and Stolte [21] indicated that a double electrode ion chamber is one of the most effective devices for obtaining absolute photoabsorption cross sections. In consideration of the earlier studies, Suzuki and Saito examined the gas-density dependence of the photoion currents from a multi-electrode ion chamber in order to remove the

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contribution of impurity photons from measured photoabsorption cross sections [20,22–24]. Kato et al. [25,26] recently applied this experimental technique to the measurements of absolute photoabsorption cross sections for Ne at the BL27SU of SPring-8, which can provide high intense photons with high energy resolution [27]. The natural lifetime width of Ne $1s^{-1}3p$ and the Ne^+ (1s) ionization threshold have been determined very accurately [26] and fine structures attributed to the inner-shell doubly excited states have been assigned in comparison with a theoretical calculation [25].

In this paper, we report the photoionization cross sections of Ar, Kr, Xe and N_2 with ultra-high resolution using the multi-electrode ion chamber. We have determined the natural lifetime widths of $2p_{3/2}^{-1}4s$, $2p_{3/2}^{-1}3d$, $2p_{3/2}^{-1}4d$ and $2p_{1/2}^{-1}4s$ resonances for Ar, $3d_{5/2}^{-1}6p$ resonance for Xe, and $1s^{-1}\pi_g^*(v'=0)$ resonance for N_2. The ionization energies to the $Ar^+(2p_{3/2}^{-1})$, $Ar^+(2p_{1/2}^{-1})$ and $Xe^+(3d_{5/2}^{-1})$ ionic states are also determined using the Rydberg formula.

2. Experimental

2.1. Apparatus

The experiments were performed using a high-resolution plane grating monochromator installed on the c-branch of the soft X-ray photochemistry beamline 27SU at SPring-8 [27]. The measurement system and experimental procedure have been described in detail elsewhere [22,23]. The monochromatized soft X-ray beam entered the multi-electrode ionization chamber of cylindrical shape, which has a window with a polyimide filter of 1100 Å thickness (LUXEL Co.). The spot size of the soft X-ray beam was about 10 μm (height) × 200 μm (width), which passes through an aperture of 1 mm diameter in front of the polyimide filter. The set of the electrodes consists of six cylinders of 5 mm diameter. The first and sixth electrodes play a role of guard rings. Photoion currents from the second to fifth electrodes were utilized for derivation of photoabsorption cross sections. Photoelectrons produced by the interaction between incident photons and the polyimide filter do not effect on the currents from the second to fifth electrodes because the produced electrons lose their energy near the filter due to collisions of gases in the ion chamber. The length of the second and third electrodes is 100 mm and that of forth and fifth 500 mm. The ionization chamber was evacuated with a turbo-molecular pump just before measurements, and supplied with a sample gas at about 0.6–400 Pa in obtaining ion currents. The ion current at each electrode was led to a calibrated picoamperemeter (Keithley, 6517) and then the data of ion currents were transferred to a personal computer. The gas density was detected with a calibrated capacitance manometer (Baratron, 690).

2.2. Photon energy calibration

The photon energy calibration was performed as follows. Well-known transition energies were used as the reference for the incident photon energy in each photoionization spectrum. The transition energy used for each spectrum is described in the corresponding section (see Sections 3.1–3.4). The dispersion of gratings in the present monochromator was determined through measurements of the Ne 1s, 2s, $2p_{1/2}$, and $2p_{3/2}$ photoelectron spectra with a high-resolution electron spectrometer (Gamma-data SCIENTA SES-2002) [28]. The photoelectron spectra were measured at the energies of both ends of energy regions available for the gratings on the monochromator. The binding energies of Ne 1s, 2s, $2p_{1/2}$, and $2p_{3/2}$ orbitals used for the dispersion calibration are 870.21 eV, 48.475 eV, 21.661 eV and 21.565 eV, respectively [29,30]. Then the dispersion for each grating has been determined in extremely high precision.

2.3. Determination of the cross section

The photoabsorption cross section measured using a double ionization chamber with ion-collection electrodes having the same length is given in principle as follows [20–22]:

$$\sigma = \frac{1}{Lp}\ln\left(\frac{i_1}{i_2}\right) = \frac{1}{L}\frac{\mathrm{d}}{\mathrm{d}p}\left(\ln\left(\frac{i_1}{i_2}\right)\right) \quad (1)$$

where p denotes the gas density, L the length of the electrodes, and i_1 and i_2 the photoion currents from the second and the third electrodes (or fourth and fifth electrodes), respectively. The gas-density dependence of the σ value obtained from Eq. (1) does not show a constant value but show appreciable scatters as we explained in the previous paper [22]. These scatters can be ascribed to incompleteness of the spectral purity of the incident photon. We analyzed the pressure dependence of the photoion current using a model, which takes into account the small contribution from stray light and higher orders [22,23]. This analysis has given a photoabsorption cross section for the first-order light accurately within an uncertainty of 1% in most photon energies.

3. Results and discussion

3.1. Ar

The photoabsorption cross section of Ar is shown as a function of incident photon energy over the energy range of 242–253 eV in Fig. 1(a). The cross section values were measured with the scan steps of 20 meV (in the energy range of 243.95–250.43 eV) and of 50 meV (below 243.95 eV and above 250.43 eV). The structures observed in Fig. 1(a) have been assigned to the $2p_{3/2}^{-1}$ *nl* and $2p_{1/2}^{-1}$ *nl* Rydberg states [31]. The Ar $2p_{3/2}^{-1}4s$ transition energy of 244.390 eV reported by King et al. [31] was used as the reference for the incident photon energy. It is seen in Fig. 1(a) that the structures attributed to $2p_{3/2} \rightarrow 4s$, 3d, 4d, 5d, 6d, 7d and $2p_{1/2} \rightarrow 4s$, 3d, 4d, 5d, 6d transitions were clearly resolved. We have analyzed the cross section curve in the range of 243–249 eV with the following expression in order to extract the line strengths, Lorentzian width for lifetime (w_L), Gaussian width for the experimental apparatus (w_G), and the energies of the resonances:

$$\sigma = \sigma_{\mathrm{dir}} + \sigma_{2p_{3/2}\rightarrow 4s} + \sigma_{2p_{1/2}\rightarrow 4s} + \sum_n \sigma_{2p_{3/2}\rightarrow nd} + \sigma_{2p_{3/2}} \quad (2)$$