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Absorbent property of fullerene for cesium isotope separation investigated using X-ray photoelectron spectroscopy

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For isotope separation of cesium (Cs)-135, the amount of Cs atom or cesium iodide (CsI) that was selectively absorbed into Buckminster-Fullerene (C₆₀) was evaluated. For C₆₀ solid surface exposed to Cs atom or CsI molecule, depth concentration profiles were investigated using angle-resolved X-ray photoelectron spectroscopy. Cs atom was found to penetrate toward C₆₀ bulk. In contrast, C₆₀ did not absorb CsI molecule into deep.

Keywords: Cesium-135; isotope separation; Buckminster-Fullerene C₆₀; X-ray photoelectron spectroscopy (XPS)

1. Introduction

Among long lived fission products, cesium-135 (¹³⁵Cs) with a half-life of 2.3 million years is an important target for nuclear transmutation next to iodine-129 and technetium-99. It has been pointed out that existence of stable isotope ¹³³Cs greatly deteriorates a net reduction of ¹³⁵Cs owing to the creation of ¹³⁵Cs by double neutron capture [1]. Thus, technological development on isotopic separation of ¹³⁵Cs from ¹³³Cs in prior to transmutation is important.

Recently, a concept of new laser isotope-selective dissociation scheme by frequency comb technique using a terahertz-wave field is proposed for diatomic molecules like cesium iodide molecule (¹³³CsI/¹³⁵CsI) in the gas-phase [2]. Thus, only ¹³⁵CsI isotope selectively dissociates to ¹³⁵Cs atom, leaving intact ¹³³CsI molecule.

However, one important requirement that still exists is the preferential recovery reaction of ¹³⁵Cs atom to ¹³³CsI, because the collision between ¹³⁵Cs atom and ¹³³CsI molecule causes isotope-exchange to form ¹³⁵CsI and ¹³³Cs [3]. Therefore, we need to develop a selective absorbent which takes only Cs atom into deep rather than CsI.

In this study, we chose Buckminster fullerene (C₆₀) as an absorbent. We investigated how Cs atom or CsI molecule was absorbed into C₆₀ using angle-resolved X-ray photoelectron spectroscopy (AR-XPS). AR-XPS is non-destructive and known to analyze depth concentration distribution at nanometer scale

corresponding to several C₆₀ molecules. We compared the absorbing property and evaluated absorbent selectivity.

2. Experiments

Experiments were performed using beamline-27A in Photon Factory of High Energy Acceleration Research Organization. Photoelectron was excited by X-rays from double-crystal monochromator with InSb(111). A detailed description of the apparatus is reported elsewhere [4]. Briefly, an analyzing chamber (base pressure 1×10^{-7} Pa) was equipped with XPS system with a spherical electron energy analyzer (VSW Co., CLASS100) and a sputter ion-gun. The preparation chamber was equipped with K-cells (AVC Co.) for C₆₀ (Aldrich Co., 99%) and CsI (Kanto Chem. Co., 99.99%), and Cs alkali metal dispenser (SAES Co., CS/NF/3.9/12FT10), a thickness monitor (INFICON Co., STM/2), and a quadrupole mass spectrometer (SRS Co., RGA200) for monitoring relative flux of Cs or CsI species during deposition. Sample films were prepared in the vacuum chamber, and transferred to the analyzing chamber that was connected to synchrotron beam-line.

Si(111) substrates were cleaned by repeated Ar⁺-sputtering. Through the K-cell heated at 750 K, C₆₀ was grown on the Si substrates. On C₆₀ films, Cs atom or CsI was dosed from the SAES getter source (Cs₂CrO₄) or CsI powder, respectively. Typical deposition rates were ca. 0.02 Å/sec (C₆₀), 0.03 Å/sec (Cs), and 0.005 Å/sec (CsI), which were recorded by the thickness monitor.

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3. Results and discussion

Figures 1a and 1b show X-ray photoelectron spectra for a Cs dosed C_{60} (hereafter, we abbreviate it as Cs/C_{60}) film and for CsI deposited on C_{60} (CsI/C_{60}), respectively, which covered Cs $3d_{5/2, 3/2}$, I $3d_{5/2, 3/2}$, and C $1s$ regions. To obtain depth concentration profiles of Cs atom, photoelectron spectra were measured at various electron emission angles (θ) defined as between the electron energy analyzer direction and the surface normal ($\theta = 0^\circ$). It was found that the angular dependence of intensity of C $1s$ relative to Cs $3d$ differed between Cs/C_{60} and CsI/C_{60} . In Figure 1b, we can see that relative C- $1s$ intensity decreased at $\theta = 68^\circ$ compared with that at $\theta = 7^\circ$.

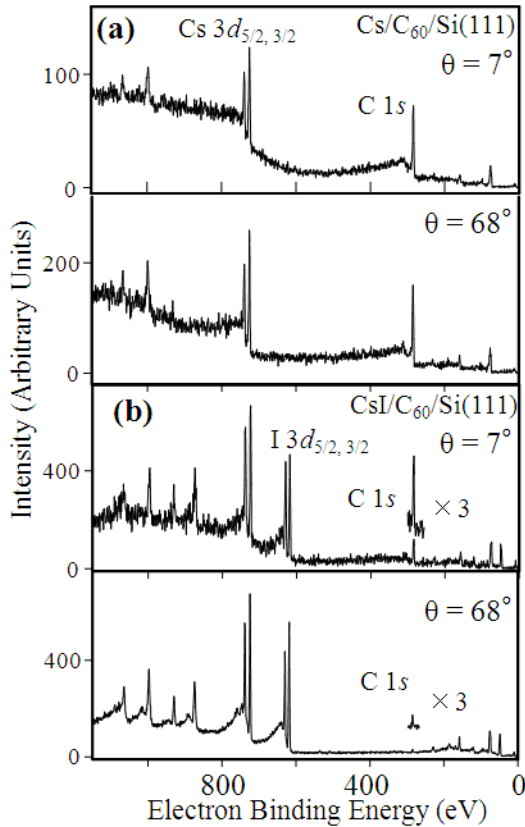


Figure 1. X-ray photoelectron spectra measured with photon energy of 2200 eV for (a) Cs-dosed on C_{60} film and for (b) CsI-deposited on C_{60} film. Electron emission angles (θ) are indicated on the right top.

This difference was further evidenced in Figure 2 that shows integrated intensities of Cs $3d_{5/2, 3/2}$ (or I $3d_{5/2, 3/2}$) and C $1s$ (labeled \times) plotted as a function of θ , although there was a trend that detection efficiencies decreased with increasing θ . Photoelectron intensities in Figure 2 were corrected by electron kinetic energy dependencies of analyzer transmission functions (F) for the equipment used and by partial photoionization cross sections (σ). The F values were determined by separately measuring standard materials. Theoretical $\sigma(Cs\ 3d_{5/2}) = 116000$, $\sigma(Cs\ 3d_{3/2}) = 81400$, $\sigma(I\ 3d_{5/2}) = 95900$, $\sigma(I\ 3d_{3/2}) = 53500$, and $\sigma(C\ 1s) = 4800$ barns for

$h\nu = 2200$ eV photon were used [5].

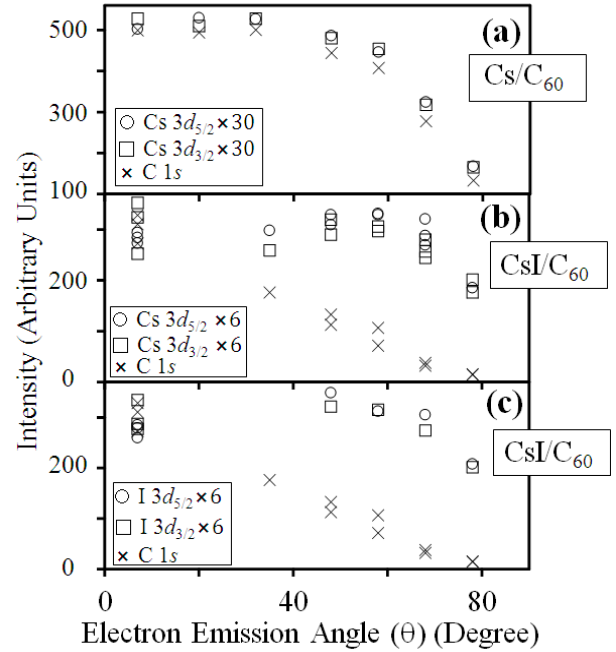


Figure 2 (a) Intensities of Cs $3d_{5/2, 3/2}$ and C $1s$ peaks as a function of electron emission angles θ , which were measured for Cs-dosed C_{60} film. Intensities of (b) Cs $3d_{5/2, 3/2}$ and C $1s$ and (c) I $3d_{5/2, 3/2}$ and C $1s$ peaks measured for CsI-deposited C_{60} film.

A key finding is the fact in Cs/C_{60} (Figure 2a) that the angular dependence of relative C $1s$ intensities (labeled \times) was not prominent and also similar to that of Cs $3d_{5/2, 3/2}$ intensities, suggesting that Cs and carbon concentration did not apparently change between shallow and deep regions for Cs/C_{60} . In contrast, as for CsI/C_{60} (Figures 2b and 2c), the relative C $1s$ intensities (labeled \times) gradually decreased by increasing θ angles. This observation can be qualitatively explained by considering that detection depths became shallow at large θ angles. Detection depth was estimated to be roughly three times of inelastic mean free path (IMFP or λ) times $\cos(\theta)$. In fact, the detection depths were calculated to be 171 Å at near the right-angle detection ($\theta = 7^\circ$) and 33 Å at the grazing detection ($\theta = 78^\circ$), on the basis of λ_{CsI} (here, λ_{CsI} denotes IMFP in which photo-electrons pass through CsI medium) of C $1s$ for $h\nu = 2200$ eV photon. So, we assume that the decrease in the C $1s$ intensity for CsI/C_{60} suggests low carbon concentration at shallow surface compared with deep.

The measured integrated intensity $I(\theta)$ at various angles θ can be expressed in the following equation [6]:

$$I(\theta) = \frac{F \cdot D \cdot K}{\cos \theta} \sigma \int_0^\infty dz f(z) \exp\left(\frac{-z}{\lambda \cos \theta}\right) \quad (1)$$

where $f(z)$ is the atomic density at depth z , D is the detection efficiency, K includes X-ray flux and other

dependencies related with the instrument. As seen in Figure 2, photoelectron intensities were strongly influenced by angular dependencies of F, D, K, and $1/\cos(\theta)$ in Eq. (1). However, such angular dependencies may be eliminated by calculating fractional intensities, e.g. $I_{Cs3d}/(I_{Cs3d} + I_{C1s})$, as a function of angles θ .

Figure 3 shows fractional intensities of Cs $3d_{5/2, 3/2}$, $I-3d_{5/2, 3/2}$, and C $1s$ for Cs/C₆₀ (Figure 3a) and CsI/C₆₀ (Figures 3b, 3c). Again, gradual dependence in Cs $3d_{5/2, 3/2}$ and C $1s$ was observed for Cs/C₆₀, while marked angular dependence was shown in Cs $3d_{5/2, 3/2}$ (or $I-3d_{5/2, 3/2}$) and C $1s$ for Cs/C₆₀. These observations consistently support the above-mentioned view that Cs was mixed into C₆₀ bulk, whilst CsI was deposited on C₆₀ surface forming over-layer.

To understand quantitatively, we postulated an over-layer model in which a uniform film was formed on the C₆₀ surface. Considering CsI thin film on C₆₀, the intensity of Cs $3d$ or C $1s$ is expressed as,

$$I(Cs 3d) = K(\theta) \sigma(Cs 3d) \lambda_{CsI}(Cs 3d) n(Cs) \left[1 - \exp\left(\frac{-d}{\lambda_{CsI}(Cs 3d) \cos \theta}\right) \right] \quad (2)$$

$$I(C 1s) = K(\theta) \sigma(C 1s) \lambda_{CsI}(C 1s) n(C) \exp\left(\frac{-d}{\lambda_{CsI}(C 1s) \cos \theta}\right) \quad (3)$$

where d is thickness of postulated CsI over-layer, $K(\theta)$ includes angular dependencies related with the instrument. Equations 2 and 3 are special cases of Eq. (1). IMFPs were calculated to be $\lambda_{CsI}(Cs 3d_{5/2, 3/2}) = 46.4 \text{ \AA}$,

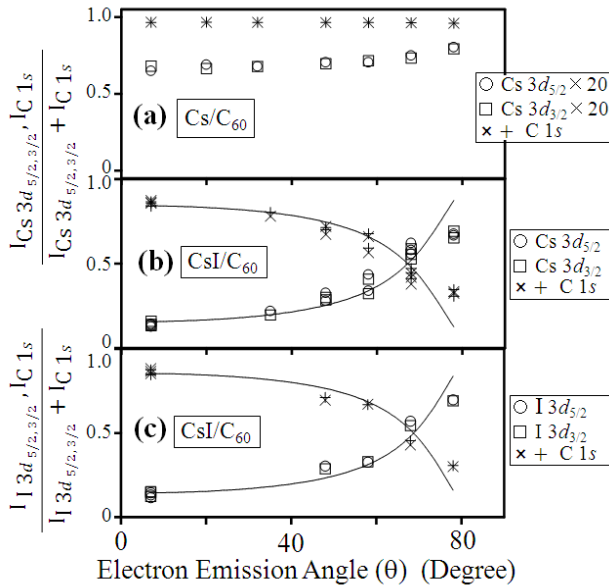


Figure 3. Fractional intensities, e.g. $I_{Cs3d}/(I_{Cs3d} + I_{C1s})$, of (a) Cs $3d_{5/2, 3/2}$ peaks as a function of electron emission angles (θ), which were measured for Cs-dosed C₆₀ film. Those of (b) Cs $3d_{5/2, 3/2}$ and (c) $I-3d_{5/2, 3/2}$ peaks measured for CsI-deposited C₆₀ film. Full lines show the best fitted curves calculated by assuming a uniform CsI-over-layered model.

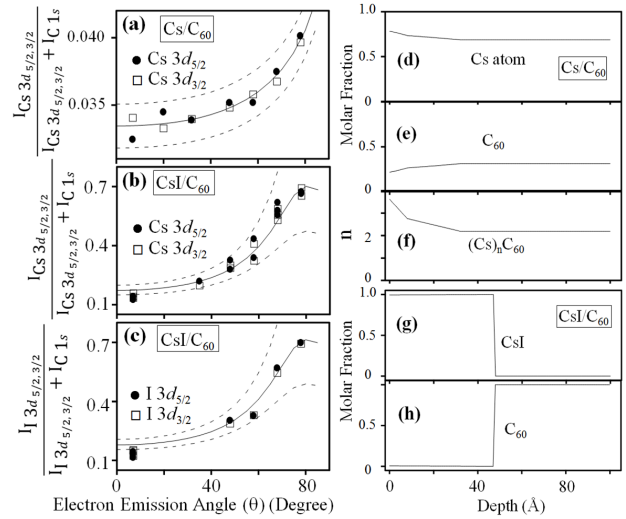


Figure 4. On the left, enlarged fractional intensity plots of (a) Cs $3d_{5/2, 3/2}$ peaks for Cs-dosed C₆₀ film, along with the best fit curves. Those of (b) Cs $3d_{5/2, 3/2}$ and (c) $I-3d_{5/2, 3/2}$ for CsI-deposited C₆₀ film. On the right, the most probable depth molar-fractional profiles (d), (e), and ratio n (f) for Cs-dosed C₆₀ film and those (g) and (h) for CsI-deposited C₆₀ film. Broken lines show curves assuming $\pm 6\%$ deviations from the best Cs molar fractions.

$\lambda_{CsI}(I-3d_{5/2, 3/2}) = 49.1 \text{ \AA}$, $\lambda_{CsI}(C 1s) = 57.2 \text{ \AA}$, $\lambda_{C60}(C 1s) = 45.2 \text{ \AA}$ for $h\nu = 2200 \text{ eV}$ based on TPP2M method [7]. Atomic densities are $n(Cs) = 1.73 \times 10^{-2}$ and $n(C) = 0.143$ [mol cm⁻³] for crystalline CsI and C₆₀, respectively. Figures 3b and 3c depict the best-fit curves which give the thickness (d) of CsI over-layer being 48 Å (Cs $3d_{5/2}$), 46 Å (Cs $3d_{3/2}$), 44 Å ($I-3d_{5/2}$), and 43 Å ($I-3d_{3/2}$) for CsI/C₆₀. It is noteworthy that Cs $3d_{5/2, 3/2}$ and $I-3d_{5/2, 3/2}$ data gave consistent thickness. As for Cs/C₆₀ (Figure 3a), on the other hand, the fitting routine could not find any suitable solutions and ended in failed error because C $1s$ intensity did not decrease by increasing angles θ . Considering the nature that Cs atoms were mixed in C₆₀ solid, it is consistent that over-layer hypothesis is not valid for Cs/C₆₀.

To understand how Cs atom penetrated into C₆₀, we tried to convert the angle-dependent photoemission intensities to molar compositions as a function of depth. We postulated a model depth profile containing concentration gradients constructed from three linear segments, which has been modeled by Paynter [6]. This model contains the quantities of concentrations c_i at the depth z_i , $i = 1, 2$, or 3. The intensity calculation takes the sum over each linear segment; that is,

$$I = I_1(c_1, z_1(=0) \rightarrow c_2, z_2) + I_2(c_2, z_2 \rightarrow c_3, z_3) + I_3(c_3, z_3 \rightarrow c_3, \infty)$$

We profiled cesium distributions by the procedure described below. First, Eq. (1) was numerically integrated assuming independent variables. Next, angular profiles of fractional intensities, e.g. $I_{Cs3d}/(I_{Cs3d} + I_{C1s})$, were calculated. Finally, the sums of weighted squares error (chi squares) were calculated,

$$\chi^2 = \sum_k \frac{(F_{r_k}^{\text{calc}} - F_{r_k}^{\text{obs}})^2}{\sigma_k^2} \quad (4)$$

where σ_k represents the standard deviation in the k -th measurement at an angle θ_k ; and $F_{r_k}^{\text{calc}}$ and $F_{r_k}^{\text{obs}}$ show calculated and experimental fractional intensities, respectively. The aforementioned calculations were repeated until the chi squares were minimized using a generalized-reduced-gradient fitting routine. In calculating Eq. (1), treating λ as constant gave qualitatively the same result. But, for accurate calculation we used the following formula in integration in the case of CsI/C₆₀,

$$\lambda_{\text{mixture}}(\text{Cs}3d) = \frac{1}{\frac{m(\text{CsI})}{\lambda_{\text{CsI}}(\text{Cs}3d)} + \frac{m(\text{C}_{60})}{\lambda_{\text{C}_{60}}(\text{Cs}3d)}} \quad (5)$$

$$\lambda_{\text{mixture}}(\text{C}1s) = \frac{1}{\frac{m(\text{CsI})}{\lambda_{\text{CsI}}(\text{C}1s)} + \frac{m(\text{C}_{60})}{\lambda_{\text{C}_{60}}(\text{C}1s)}} \quad (6)$$

where $m(\text{CsI})$ and $m(\text{C}_{60})$ are molar fractions. In the case of Cs/C₆₀, $\lambda_{\text{mixture}}(\text{Cs}3d)$ and $\lambda_{\text{mixture}}(\text{C}1s)$ in integration of Eq. (1) were taken as a function of depth z and calculated based on TPP2M formulae with densities that were corrected considering an approximate linear relation between molecular weight of Cs_{*n*}C₆₀ and its density under $n < 8$ [8].

Figures 4 a-c show the best fitted fractional intensity curves. **Figures 4 d-h** show the obtained depth profiles of molar fractions for Cs or CsI versus C₆₀, e.g. $[\text{Cs}]/([\text{Cs}]+[\text{C}_{60}])$. It is well-known that depth profile is not uniquely determined from a set of experimental data [6]. Even so, different characteristics were clearly obtained between Cs/C₆₀ and CsI/C₆₀. As for Cs/C₆₀, concentration $c_3(\text{Cs})$ ($= 0.68$, molar fraction, i.e., $[\text{Cs}]/([\text{Cs}]+[\text{C}_{60}])$) at z_3 ($= 32 \text{ \AA}$) $\rightarrow \infty$ tended to be close to $c_2(\text{Cs})$ ($= 0.73$) at z_2 ($= 8 \text{ \AA}$), indicating that the Cs concentration was maintained into deep bulk as shown in Figure 4d. We found in Figure 4f that as typical ratio Cs_{3.6}C₆₀ at surface and Cs_{2.2}C₆₀ at bulk were estimated for Cs/C₆₀. In contrast, as for CsI/C₆₀ the concentration $c_3(\text{CsI})$ ($= 0.0$, i.e., $[\text{CsI}]/([\text{CsI}]+[\text{C}_{60}])$) at z_3 ($= 47 \text{ \AA}$) tended to be nearly zero, as shown in Figure 4g. Although a certain amount of CsI was deposited on the C₆₀ surface, we consider that CsI molecule did not penetrate into bulk but stopped at a barrier interface between CsI and C₆₀ phases.

4. Conclusion

We investigated the property of C₆₀ solid as an absorbent for Cs atom or CsI molecule using the angle-resolved XPS technique. Unusual angular independencies were observed for Cs-dosed C₆₀, while over-layer-like ordinary angular dependencies were

recorded for CsI-deposited C₆₀. This observed difference was interpreted as the different penetrating abilities between Cs and CsI into the C₆₀ solid. Thus, the present results show that C₆₀ may become a candidate for Cs-selective absorbent material that prevents ¹³⁵Cs and ¹³³CsI from collision. For realizing the ideal situation that CsI does not stick on the C₆₀ surface, experiments with heating substrates are in progress.

Acknowledgements

The authors wish to thank Drs. Y. Okamoto and I. Shimoyama of JAEA, Prof. N. Usami and the staff of Photon Factory KEK for the helpful support during synchrotron experiments performed under PF-PAC (No. 2016G-188). This work was supported by JSPS KAKENHI [grant number 15H02345].

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