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 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 131Cs [3]. Therefore, we need to develop a selective absorbtion 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 (INFINICON 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 doped 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 3$d_{5/2,3/2}$, I 3$d_{5/2,3/2}$, and C 1$s$ regions. To obtain depth concentration profiles of Cs atom, photoelectron spectra were measured at various electron emission angles ($\theta$) 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 1$s$ relative to Cs 3$d$ differed between Cs/C$_{60}$ and CsI/C$_{60}$. In Figure 1b, we can see that relative C-1$s$ intensity decreased at $\theta = 68^\circ$ compared with that at $\theta = 7^\circ$.

This difference was further evidenced in Figure 2 that shows integrated intensities of Cs 3$d_{5/2,3/2}$ and C 1$s$ peaks as a function of electron emission angles $\theta$, which were measured for Cs–dosed C$_{60}$ film. Intensities of (b) Cs 3$d_{5/2,3/2}$ and C 1$s$ and (c) I 3$d_{5/2,3/2}$ and C 1$s$ 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 1$s$ intensities (labeled $\times$) was not prominent and also similar to that of Cs 3$d_{5/2,3/2}$ 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 1$s$ intensities (labeled $\times$) gradually decreased by increasing $\theta$ angles. This observation can be qualitatively explained by considering that detection depths became shallow at large $\theta$ angles. Detection depth was estimated to be roughly three times of inelastic mean free path (IMFP or $\lambda$) 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 $\lambda_{CsI}$ (here, $\lambda_{CsI}$ denotes IMFP in which photo-electrons pass through CsI medium) of C 1$s$ for $h\nu = 2200$ eV photon.

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

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

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(θ) in Eq. (1). However, such angular dependencies may be eliminated by calculating fractional intensities, e.g., \( I_{C60}/(I_{C60} + I_{C1s}) \), as a function of angles θ.

Figure 3 shows fractional intensities of Cs 3d_{5/2,3/2}, 1s for Cs/C_{60} (Figure 3a) and CsI/C_{60} (Figures 3b, 3c). Again, gradual dependence in Cs 3d_{5/2,3/2} and 1s was observed for Cs/C_{60}, while marked angular dependence was shown in Cs 3d_{5/2,3/2} (or 1s) for CsI/C_{60}. Moreover, the results confirm that relative C 1s intensity decreased by increasing angles θ. These observations consistently support the above-mentioned view that Cs was mixed into C_{60} bulk, whilst CsI was deposited on C_{60} surface forming over-layer.

To understand quantitatively, we postulated an over-layer model in which a uniform film was formed on the C_{60} surface. Considering CsI thin film on C_{60}, the intensity of Cs 3d or 1s is expressed as

\[
I(\text{Cs3d}) = K(\theta) \sigma(Cs3d) \lambda_{cs}(Cs3d) n(Cs) \exp\left(-\frac{d}{\lambda_{cs}(Cs3d) \cos\theta}\right) \tag{2}
\]

\[
I(1s) = K(\theta) \sigma(1s) \lambda_{cs}(1s) n(C) \exp\left(-\frac{d}{\lambda_{cs}(1s) \cos\theta}\right) \tag{3}
\]

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 \( \lambda_{cs}(Cs3d_{5/2,3/2}) = 46.4 \, \text{Å} \), \( \lambda_{cs}(C1s) = 45.2 \, \text{Å} \) for hν = 2200 eV based on TPP2M method [7]. Atomic densities are \( n(Cs) = 1.73 \times 10^{23} \, \text{mol}^{-2} \) and \( n(C) = 0.143 \, \text{mol}^{-2} \) for crystalline CsI and C_{60}, respectively. Figures 3b and 3c depict the best-fit curves which give the thickness (d) of CsI over-layer being 48 Å (Cs I_{3/2}), 46 Å (Cs 3d_{5/2}), 44Å (1s), and 43 Å (1s) for CsI/C_{60}. It is noteworthy that Cs 3d_{5/2,3/2} and (1s) for CsI-deposited C_{60} film. Broken lines show curves assuming ±6% deviations from the best Cs molar fractions.

\[
\lambda_{cs}(1s) = 49.1 \, \text{Å}, \lambda_{cs}(C1s) = 57.2 \, \text{Å}, \lambda_{cs}(C3d_{s}) = 45.2 \, \text{Å} \text{ for } h\nu = 2200 \, \text{eV based on TPP2M method [7].}
\]

To understand how Cs atom penetrated into C_{60}, 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,

\[
I = I_c(c_i, z_i) = I_{cs}(c_i, z_i) + I_{cs}(c_i, z_i) + I_{cs}(c_i, z_i)
\]

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.

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**Figure 2.** Electron emission angle dependence of photoelectron 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 C_{60} film. Those of (b) Cs 3d_{5/2,3/2} and (c) 1s peaks measured for CsI-dosed C_{60} film. Full lines show the best fitted curves calculated by assuming a uniform CsI-over-layered model.
\[ \chi^2 = \sum_k \frac{(F_{k}^{exp} - F_{k}^{calc})^2}{\sigma_k^2} \]  

where \( \sigma_k \) represents the standard deviation in the k-th measurement at an angle \( \theta_k \); and \( F_{k}^{calc} \) and \( F_{k}^{exp} \) 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 \( \lambda \) as constant gave qualitatively the same result. But, for accurate calculation we used the following formula in integration in the case of Cs/C\(_{60}\).

\[ \lambda_{mixture}(Cs3d) = \frac{1}{\lambda_{Cs}(Cs3d) + \lambda_{C60}(Cs3d)} \]  

(5)

\[ \lambda_{mixture}(C1s) = \frac{1}{\lambda_{Cs}(C1s) + \lambda_{C60}(C1s)} \]  

(6)

where \( m(Cs) \) and \( m(C60) \) are molar fractions. In the case of Cs/C\(_{60}\), \( \lambda_{mixture}(Cs3d) \) and \( \lambda_{mixture}(C1s) \) in integration of Eq. (1) were taken as a function of depth \( z \) and calculated based on PPP2M formulae with densities not uniquely determined from a set of experimental data [6]. Even so, different characteristics were clearly obtained between Cs/C\(_{60}\) and CsI/C\(_{60}\). As for Cs/C\(_{60}\), concentration \( c_{2}(Cs) = 0.68 \), molar fraction, i.e., \( [Cs]/([Cs]+[C60]) \) at \( z_{2} = 32 \text{ Å} \) tended to be close to \( c_{3}(Cs) = 0.73 \) at \( z_{3} = 8 \text{ Å} \), 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\(_{1.8}\)/C\(_{60}\) at surface and Cs\(_{2.2}\)/C\(_{60}\) at bulk were estimated for Cs/C\(_{60}\). In contrast, as for CsI/C\(_{60}\) the concentration \( c_{2}(CsI) = 0.0 \), i.e., \( [CsI]/([CsI]+[C60]) \) at \( z_{2} = 47 \text{ Å} \) tended to be nearly zero, as shown in Figure 4g. Although a certain amount of CsI was deposited on the C\(_{60}\) surface, we consider that CsI molecule did not penetrate into bulk but stopped at a barrier interface between CsI and C\(_{60}\) phases.

4. Conclusion

We investigated the property of C\(_{60}\) solid as an absorbent for Cs atom or CsI molecule using the angle-resolved XPS technique. Unusual angular independencies were observed for Cs-dosed C\(_{60}\), while over-layer-like ordinary angular dependencies were recorded for CsI-deposited C\(_{60}\). This observed difference was interpreted as the different penetrating abilities between Cs and CsI into the C\(_{60}\) solid. Thus, the present results show that C\(_{60}\) may become a candidate for Cs-selective absorbent material that prevents \(^{133}\)Cs and \(^{137}\)CsI from collision. For realizing the ideal situation that CsI does not stick on the C\(_{60}\) surface, experiments with heating substrates are in progress.

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