# X-ray Photoelectron Spectroscopy and Ab Initio Molecular-Dynamics Studies of an Air-Exposed $C_{60}$ Film

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X-ray photoelectron spectra of $C_{60}$ films exposed to air of *ca.* 20 % and 60 % humidity at 23 °C for 1 h are presented. It was found that the O 1s core peak appeared at a binding energy of 533.5 eV for the film exposed to air of *ca.* 60 % humidity, while no peak corresponding to the O 1s photoelectrons was observed for the film exposed to air of *ca.* 20 % humidity. The binding energy of 533.5 eV for the O1s core peak is close to that of about 533 eV for the O1s core peak of solid $H_2O$, while it is different from that of 537 eV for the O 1s core peak of solid $O_2$ on $C_{60}$ film. These facts indicate that the O 1s peak observed for the air-exposed $C_{60}$ film was due to $H_2O$ molecules adsorbed on the film. The adsorption state of $H_2O$ molecules on the $C_{60}$ molecule is discussed on the basis of the results obtained using first-principle molecular dynamics calculations within a local density approximation.
Key words: XPS, $C_{60}$ film, O 1s core peak, first-principle molecular-dynamics calculations

## 1. INTRODUCTION

Since the discovery of an effective production method for $C_{60}$ [1], there have been many reports on the electronic properties of pristine and metal-doped $C_{60}$ films applied to functional devices. In this field, the interaction between $C_{60}$ and molecular gases, in particular air ($O_2$, $N_2$, and $H_2O$), is one of the most important subjects from the viewpoint of $C_{60}$-based materials. For example, the effect of air on the resistivity [2,3] and photoconductivity [4-6] of $C_{60}$ films has been reported by several groups and it was found that $O_2$ molecules markedly affected these properties, while the effect of $N_2$ molecules was negligible. This indicates that the interaction between $C_{60}$ and $N_2$ does not have to be considered in the air-exposed $C_{60}$ films. On the other hand, water vapor can be adsorbed on the film as well as $O_2$ molecules and this should be considered. However, little attention has been paid to the interaction between $C_{60}$ and $H_2O$ until now, although there have been many experimental [7-18] and theoretical [19-22] reports on the interaction between solid $C_{60}$ and various gases such as $O_2$, $N_2$, CO, Ar, and He. The aim of the present work is to study the interactions between $C_{60}$ and $O_2/H_2O$ molecules for the $C_{60}$ films exposed to air of moderate humidity at a given temperature using X-ray photoelectron spectroscopy (XPS) [23] in combination with first-principle molecular-dynamics calculations [24].

## 2. EXPERIMENT

The details of the $C_{60}$ film preparation has been described elsewhere [25]. Thin films of $C_{60}$ were deposited on a Au-(more than 1 mm thick) coated stainless steel substrate. The thickness of the $C_{60}$ film was estimated to be about 100 nm.

After deposition of the $C_{60}$ film on the substrate, this sample was taken out of the vacuum chamber and exposed to air of moderate humidity (*ca.* 20 % and 60 %) at 23 °C for 1 h prior to introducing it into an

XPS apparatus (VG: Escalab Mk-II). Humidity in the experimental room was controlled using both an air conditioner and a supersonic water vapor generator, and it was monitored using a thermohydrograph (Sato Keiryoki Co., Ltd.). Room temperature was also maintained at 23 °C using the air conditioner.
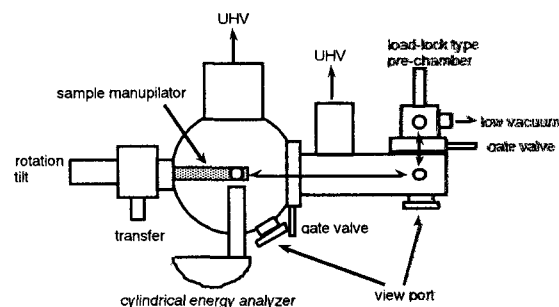


Figure 1. Schematic representation of an apparatus for the study of air-exposed $C_{60}$ film by x-ray photoelectron spectroscopy.

Figure 1 shows a schematic representation of an XPS system for the study of the air-exposed $C_{60}$ film. Three vacuum chambers are separated by two gate valves. The main chamber is equipped with an utrahigh vacuum pumping system, an X-ray source (MgK$\alpha$: 1253.6 eV), an energy analyzer (the energy resolution for the full width at half maximum of the Ag $3d_{5/2}$ is 0.6 eV), and a five-axis sample manipulator (X, Y, Z, rotation, tilt). The base pressure of this vacuum chamber was $5 \times 10^{-10}$ Torr. By rotating the sample holder, the incident angle of photoelectrons emitted from the sample into the analyzer was adjusted to 90°. The second chamber is also a UHV system similar to that of the main chamber and is equipped with a system for sample transfer from this chamber to the main chamber. The third chamber is a load-lock prechamber equipped with a low vacuum system ($10^{-3}$ Torr) for introducing the sample into the second

chamber.

Various XPS data handling such as smoothing, background removal and peak fitting were carried out by a Fisons analysis software package (ECLIPS). The Au $4f_{7/2}$ (83.7 eV) transition was used as a reference peak for estimation of the binding energy of other peaks.

We measured the XPS spectra between the center and edge of the sample area. When we compared the binding energy of the C 1s core peak observed for the center area with that for the edge area, both C 1s core peaks had the same binding energy (284.7 eV). This shows that there was no effect of charge-up on the sample upon X-ray irradiation. The substrate temperature was maintained at room temperature during XPS measurement.

## 3. COMPUTATIONAL METHOD

We used a self-consistent mixed-basis full-potential method for the calculation of $C_{60}$-gas interactions. A combined set of plane waves and Bloch sums of localized functions is employed as basis functions, thus leading to a very efficient representation of the system containing both highly localized and delocalized electrons. The present method is based on the density-functional theory with local density-functional approximation.

For the basis set of $C_{60}$, 60 1s and 60 $2p_x$, 60 $2p_y$, 60 $2p_z$ atomic orbitals and 2109 plane waves are adopted. The exponential damping factors $\alpha$ and $\beta$ for the 1s and 2p atomic wave functions were chosen to be 1/0.106 and 1/0.133 $\text{Å}^{-1}$, respectively. The real space was divided into 64×64×64 meshes where 3.185 meshes correspond approximately to 1 a.u. = 0.529 Å. The details of this method has been described elsewhere [24].

## 4. RESULTS AND DISCUSSION

Figure 2 shows the XPS spectrum in the binding energy range of 0-1000 eV for the $C_{60}$ film exposed to air of *ca.* 20 % humidity at 23 °C for 1 h. It is interesting to note that no peak corresponding to the O 1s photoelectrons (530-540 eV) was observed below a detection limit of less than 0.1-At % in the present XPS system. The reproducibility of this result was confirmed by obtaining the XPS spectrum under similar conditions.

We estimated the escape depth of the C1s photoelectrons using a modified Bethe equation[26] and found it to be about 54 Å. Since the $C_{60}$ film has a fcc structure with a lattice constant of 14.17 Å [27] at room temperature and the mean ball diameter of a $C_{60}$ molecule is 7.10 Å [28], the present XPS spectra provided information on almost four unit cells below the film surface. Furthermore, the escape depth of the O 1s photoelectrons is on the same order as that of C 1s photoelectrons [29]. This suggests that oxygen atoms were not present not only on the surface of the

air-exposed $C_{60}$ film but also within four unit cells below the surface.
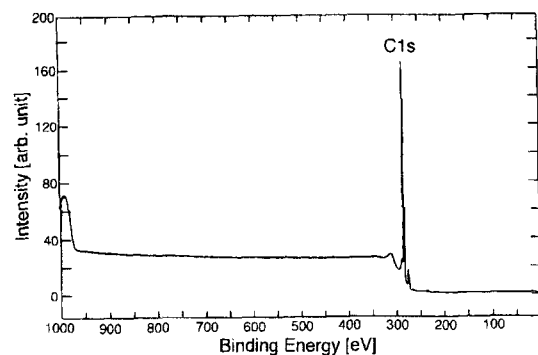


Figure 2. X-ray photoelectron spectrum in the binding energy range of 0-1000 eV for the $C_{60}$ film exposed to air of ca. 20% humidity at 23 °C for 1 h.

When a $C_{60}$ film was exposed to air of *ca.* 60% humidity at 23 °C for 1 h, the O1s peak was first detected. These facts suggest that the O1s core peak was attributed not to $O_2$ molecules but to $H_2O$ molecules adsorbed on the $C_{60}$ film. Figure 3 shows the photoelectron spectrum of the O1s for the film exposed to air of high humidity in the binding energy range of 520-550 eV. It was found that the O1s core peak appeared at a binding energy of 533.5 eV. Kroll et al. [8] have reported XPS spectra of solid $O_2$ adsorbed on a $C_{60}$ film at 20 K and found that the binding energy of the O1s core peak for the solid $O_2$ was about 537 eV (543-544 eV for free $O_2$ in Ref.30), which is different from our result. On the other hand, the binding energy of the O1s core peak for solid $H_2O$ has been reported to be about 533 eV (539.7 eV for free $H_2O$ in Ref.30), which is in good agreement with our result.
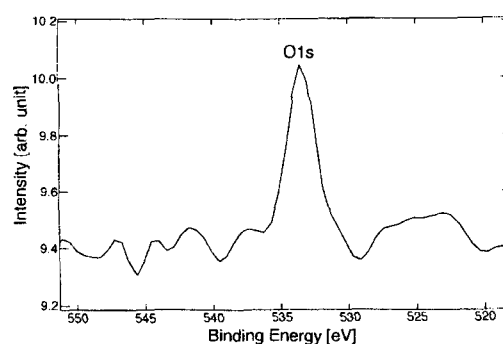


Figure 3. The photoelectron spectrum of the O1s in the binding energy range of 520-550 eV for the C60 film exposed to air of ca. 60% humidity at 23 °C for 1 h.

From the XPS intensities of the O1s and C1s peaks, the amount of oxygen was estimated to be 1.8-At %, while the amount of carbon to be 98.2-At %. This corresponds numerically to that one $H_2O$ molecule is adsorbed on one $C_{60}$ molecule within 54 Å depth of the $C_{60}$ film. However, this conclusion is hard to be accepted by the following reasons. The

activation energy for $O_2$ diffusion into the $C_{60}$ bulk lattice has been estimated to be 180 meV [5]. The molecular size of a $H_2O$ molecule (about 3 Å) is greater than that of an $O_2$ molecule (2.4 Å) and the distance between adjacent $C_{60}$ molecules is 3 Å in the fcc bulk structure, so that the activation energy for $H_2O$ diffusion into the bulk lattice is expected to be larger than that for $O_2$ molecules. Since the thermal translational energy of a molecule is about 38 meV at 23 °C, it is speculated that $H_2O$ molecules diffuse only slightly into the bulk lattice under the present conditions. From these reasons, a few solid $H_2O$ layers are assumed to be formed on the $C_{60}$ film exposed to air of high humidity at 23 °C. Consequently, the present O1s core peak originates from the $H_2O$ layers adsorbed on the air-exposed $C_{60}$ film. In addition, because the present experiments have been carried out without photoirradiation, the O1s core peak observed in Fig. 3 does not arise from photochemical products such as CO (535.7 eV), $CO_2$ (534.5 eV), and other carbonyl (532.8 eV) compounds formed on the $C_{60}$ film [9]. Indeed, Wohlers et al. [31] have recently reported on the reaction of $C_{60}$ and $C_{70}$ with molecular oxygen using X-ray absorption and photoelectron spectroscopy. When $C_{60}$ films (50-100 nm thick) were exposed to 500 mbar of oxygen for 5 min at 300 K (27 °C), no oxygen content could be observed by near edge X-ray absorption spectroscopy, as shown in Fig.1 in Ref.31. This demonstrated that molecular oxygen is unlikely to be adsorbed on the $C_{60}$ films at 300 K. This is consistent with our present results.

The XPS results suggest that $H_2O$ is physisorbed on $C_{60}$. We next disucss the interaction between $H_2O$ and $C_{60}$. Previously, Williams et al. [21] estimated the intermolecular energy between $C_{60}$ and various gas molecules such as $O_2$ and $H_2O$ by semi-empirical calculations based on atom-atom potentials. They found that the $C_{60}$-$O_2$ binding energy was -1.13 to -1.35 kcal/mol (-49.0 to -58.5 meV). Since the translational energy of a molecule at 300 K is about 40 meV, their result predicts that $O_2$ molecules are easily desorbed from $C_{60}$ films at room temperature and can explain our present results. On the other hand, the $C_{60}$-$H_2O$ binding energy was -1.06 to -1.25 kcal/mol (-46 to -54.2 meV) in their report. This predicts that $H_2O$ is more easily desorbed from $C_{60}$ films than $O_2$ at room temperature, which is in conflict with our results. Williams *et al.* calculated these interactions using an atom-atom potential expressed as the form, $A\exp(-Br) - Cr^{-6}$, where $A$, $B$, and $C$ denote constants and $r$ represents an interatomic distance. The first and second terms represent the repulsive exchange and the attractive dispersion interactions, respectively. However, besides these terms, it is important to consider the electrostatic and induction terms for the accurate estimation of the intermolecular interactions [32,33]. Indeed, $H_2O$ molecules are electronically polarized and have a permanent dipole moment in the molecule. This implies that the bonding energy due to the electrostatic and induction interactions for the $C_{60}$-$H_2O$ system becomes more significant than that for

the $C_{60}$-$O_2$ system. Thus $H_2O$ molecules are expected to be more strongly bound to the $C_{60}$ film than $O_2$ molecules.

In order to understand the interaction between $C_{60}$ and $H_2O$ molecules more satisfactorily, we examine the bonding energy between $C_{60}$ and $H_2O$ molecules using the *ab initio* molecular-dynamics calculations based on density-functional theory [24]. Prior to discussing the adsorption state of $H_2O$ on $C_{60}$, we compare the chemical shift in the O1s binding energy between experimental and theoretical results in order to confirm the reliability of the present calculations. The O1s energy shift of $H_2O$ before and after adsorption was theoretically estimated to be 4.43 eV, while that was experimentally obtained to be 6.23 eV. This discrepancy is due to the fact that present calculations do not consider the interaction between adjacent $H_2O$ molecules.

Figure 4 shows the equilibrium configuration for the adsorption state of $H_2O$ molecule on the $C_{60}$. We found that $H_2O$ molecule is adsorbed above the hexagon of $C_{60}$ by about 3.0 Å. The bonding energy between these molecules is estimated to be 0.38 eV, which is comparable to that for hydrogen bonding. This indicates that $H_2O$ molecules are more strongly physisorbed on the $C_{60}$ molecule than $O_2$ molecules. As shown in Fig. 4, it is interesting to note that the hydrogen atoms of $H_2O$ face to the hexagon of $C_{60}$.
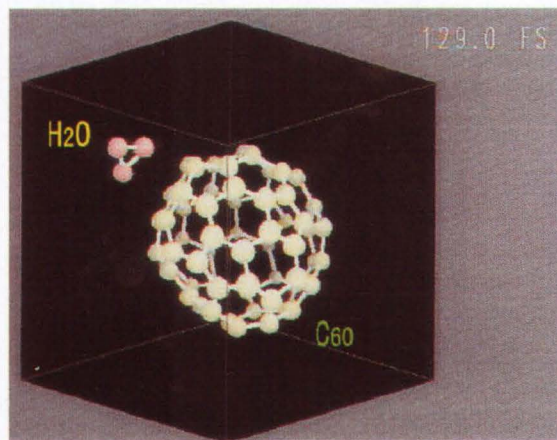


Figure 4. The equilibrium structure of $H_2O$ adsorbed on $C_{60}$ obtained using ab initio molecular-dynamics calculations. The two hydorgen atoms of $H_2O$ face the hexagon of $C_{60}$.

## 5. SUMMARY

X-ray photoelectron spectra of the $C_{60}$ films exposed to air of moderate humidity of about 20 % and 60 % at 23 °C for 1 h were presented. It was found that the O1s core peak appeared at a binding energy of 533.5 eV for the film exposed to air of *ca.* 60 % humidity, while no peak corresponding to the O1s photoelectrons was observed for the film exposed to air of *ca.* 20% humidity. The binding energy of 533.5 eV for the O1s core peak was close to that of about 533

eV for the O1s photoelectrons of solid $H_2O$, while it was different from that of 537 eV for the O1s photoelectons of solid $O_2$ on $C_{60}$ film. Consequently, the O1s core peak was assigned to $H_2O$ layers adsorbed on the $C_{60}$ film. Ab initio molecular-dynamics calculations of the $C_{60}$-$H_2O$ system found that $H_2O$ molecule is physisorbed above the hexagon of $C_{60}$ by about 3.0 Å forwarding its hydrogen atoms to this hexagon.

## ACKNOWLEDGMENTS

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