Configurations of Benzene and Pyridine Molecules Adsorbed on Graphitic Surface of Microporous Carbon

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The possible configurations of benzene and pyridine molecules adsorbed in microporous carbon were analyzed by synchrotron-radiation-excited soft X-ray emission spectroscopy and by analyzing its spectral features using DV-Xα molecular orbital calculations. The distances between the adsorbed molecules and the graphitic surface were estimated to be approximately 0.33 nm in both benzene- and pyridine-adsorbed systems. Both molecular orientations were also estimated to be almost parallel to the graphitic surface of microporous carbon. The electronic states of benzene and pyridine molecules adsorbed on the graphitic surface were similar to those of individual nonadsorbed free molecules. Therefore, the adsorption of benzene and pyridine molecules in the microporous carbon can be confirmed to be physisorption, and there is little charge-transfer between the adsorbed molecules and the graphitic surface.

1. Introduction

The configuration and electronic structures of molecular adsorbates on micropore surfaces in porous materials have attracted much attention in terms of both surface science and industrial applications.† Activated carbon, which can be regarded as a typical microporous material, has been widely utilized as an adsorbent in many industrial fields. Environmental applications constitute some of the most important uses of activated microporous carbon because it has the capacity to adsorb large amounts of many organic compounds. These applications include the treatment of water to remove organic pollutants and as an air-pollution condenser to concentrate organic pollutants in gas sensors.‡ For such environmental applications of microporous carbon, it is important to understand the configuration and electronic structures of molecular adsorbates on micropore surfaces. Many molecular adsorbates on ideal surfaces, such as metals and graphite, have been extensively investigated using surface sensitive spectroscopic methods§ including photoelectron spectroscopy (PES), the near edge X-ray absorption fine structure (NEXAFS) method, and photoelectron diffraction. However, we can obtain little information on the configuration and electronic structures of molecular adsorbates in microporous carbon because of the technical difficulties involved in the in situ direct observation of molecular adsorbates in bulk matrices.

The direct observation of molecular adsorbates in microporous materials requires the use of spectroscopic methods that have bulk-sensitivity, high-resolution, and high-efficiency.¶ One suitable method is soft X-ray emission spectroscopy using highly brilliant synchrotron radiation,¶ because of the longer transmission length of soft X-rays in solid matter. This approach can also be used to analyze both conducting and insulating materials, because the X-ray emission process is unaffected by the electrical charge of the target materials. In a previous study,¶ we provided unprecedented examples of in situ direct observations of adsorbate benzene and pyridine molecules in microporous carbon using synchrotron-radiation-excited soft X-ray emission spectroscopy. Our measurements of the C K X-ray emission spectra of benzene- and pyridine-adsorbed microporous carbon revealed differences between the spectral features of the adsorbate benzene and pyridine molecules, and the X-ray spectra agreed closely with their corresponding calculated C2p density of states (DOS) spectra. However, we observed some fine differences between the spectral features of the measured C K X-ray emission spectra and the calculated C2p-DOS spectra. We therefore decided to determine the configuration of the adsorbate molecules and their electronic interaction with the micropore surfaces in microporous carbon by using the more accurate spectral feature analysis.

In this paper, we describe the possible configurations of benzene and pyridine adsorbed in the microporous carbon, which we estimated by analyzing the spectral features of the measured X-ray emission spectra of benzene- and pyridine-adsorbed microporous carbon with their theoretically obtained DOS spectra, in relation to the electronic interaction between the adsorbed molecules and the micropore surface in microporous carbon.

2. Experiment

Benzene- and pyridine-adsorbed microporous carbon samples were prepared by covering commercially obtained activated carbon powders (100 mesh, Darco§, G-60) with benzene and pyridine solvents, respectively, and then drying them at room temperature. Spectroscopic measurements of X-ray emissions in the C K and N K regions were performed at the third-generation synchrotron radiation facility of Advanced Light Source (ALS). The X-ray emission spectra were measured using a grating X-ray spectrometer installed in a beamline (BL) 8.0.¶

References

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![Graph of Benzene and Pyridine Molecules](image)

**Figure 1.** C K X-ray emission spectra of the benzene-adsorbed microporous carbon system. The upper panel shows the C K X-ray emission spectra of (A) benzene-adsorbed microporous carbon and (B) untreated microporous carbon. The lower panel shows the spectrum remaining after subtracting (B) from (A), which corresponds to the X-ray emission spectrum of adsorbate benzene molecules in the microporous carbon. Superimposed is the calculated C2p DOS spectrum of a benzene molecule broadened with 0.5-ev–fwhm Lorentzian functions.

The experimental details are described elsewhere. Because we expected the C K X-ray emission from the microporous carbon matrix to exhibit a huge background relative to the emissions from the adsorbate benzene and pyridine molecules, we measured the C K X-ray signals of benzene-adsorbed microporous carbon, pyridine-adsorbed microporous carbon, and untreated microporous carbon for about 7 h each, to obtain a large enough signal-to-noise (SN) ratio to ensure the spectra of these aromatic molecular adsorbates were reliable.

We undertook the theoretical spectral feature analysis by using discrete variational (DV) Xα molecular orbital calculation, which can generally well reproduce the K-V X-ray emission spectra of carbon and nitrogen from their ground state 2p DOSs. The calculations were made using the SCAT program in commercially obtained DV-Xα software on a DOS/V computer. We used the basis set of 1s, 2s, and 2p orbitals for both carbon and nitrogen atoms. We also obtained optimized geometries of benzene and pyridine adsorbed on the graphitic surface of microporous carbon by the TINKER method with MM3 force fields parameters.

3. Results and Discussion

3.1 X-ray Emission Spectra. Figure 1 shows the C K X-ray emission spectra of the benzene-adsorbed microporous carbon system. The upper panel shows the C K X-ray emission spectra of (A) benzene-adsorbed microporous carbon and (B) untreated microporous carbon, which were normalized at the background intensity observed in energy regions higher than 285 eV. The spectral features of the untreated microporous carbon, which consisted of a main peak near 278 eV with a low-energy tail and a high-energy shoulder near 282 eV, are in good agreement of those of graphite powder. This shows that the local molecular structure of the microporous carbon is similar to that of graphite. The maximum peak intensity of the benzene-adsorbed microporous carbon was more than 360 000 counts, and the S/N ratio seemed to be sufficient for obtaining the X-ray spectrum of benzene molecules adsorbed in the microporous carbon, as described later. We observed little difference between the spectral features of the benzene-adsorbed and the untreated microporous carbon. This shows that the concentration of adsorbate benzene molecules in the microporous carbon may be of the order of a few percent.

To obtain the X-ray emission spectrum of the adsorbate benzene molecules in the microporous carbon, we subtracted the spectrum of the untreated microporous carbon from that of benzene-adsorbed microporous carbon. The remaining spectrum (A)−(B) is shown in the lower panel. It has a sharp main peak at 278 eV with a low-energy tail and a high-energy peak at 283 eV. Superimposed on it is the calculated C2p density of states (DOS) spectrum of a benzene molecule broadened with 0.5-eV–fwhm (full width at half-maximum) Lorentzian functions. We obtained this C2p-DOS spectrum by discrete variational (DV)-Xα molecular orbital calculation. Major peaks in this spectrum are denoted by a to g in the figure. The spectral features of this calculated C2p-DOS are in good agreement with those of the C K X-ray emission spectrum of benzene molecules published elsewhere. A comparison of the subtracted X-ray spectrum (A)−(B) with the calculated C2p-DOS spectrum shows that the spectral features of the X-ray spectrum are similar to those of the calculated spectrum; the high-energy peak at 283 eV corresponds to peak a in the calculated spectrum, the main peak at 278 eV to b and c, and the low-energy tail to d to g. Therefore, the subtracted X-ray spectrum (A)−(B) is probably due to the adsorbate benzene molecules. This also demonstrates the feasibility of the direct observation of benzene molecules adsorbed in microporous carbon by soft X-ray emission spectroscopy. We assume that the C K emission yields of adsorbed benzene and of microporous carbon are almost the same, because the electronic structures of benzene and microporous carbon are both similar to that of graphite powder. Therefore, the area ratio of the emission spectrum for benzene can be calibrated using the ratio of total number of carbon atoms in benzene and in microporous carbon. The area ratio difference [(A)−(B)]/(B) is about 8% here. This shows that the area occupied per benzene molecule is larger than twelve aromatic rings of microporous carbon, the latter being about 1.50 nm². The cross-section of a benzene molecule is about 0.4 nm², thus all of the benzene is considered to be adsorbed as a monolayer on the graphitic surface of microporous carbon. Furthermore, before the spectroscopic analysis, we measured the nitrogen isotherm of this microporous carbon at 77 K with a BELSORP TCV automatic gas adsorption apparatus (BEL Japan, Inc.) to investigate the porosity of the microporous carbon. According to the analysis of the measured isotherm using the microporous (MP) method, the radii of micropores were distributed between 0.4 nm to 0.7 nm; the mode radius was 0.42 nm. This shows that the greater part of the adsorbed benzene is in the form of a flat monolayer, even under a high partial pressure of benzene. Thus, the X-ray difference spectrum (A)−(B) is most probably due to the monolayer of adsorbed benzene molecules. However, we observed some fine differences between the spectral shapes of the subtracted X-ray spectrum (A)−(B) and the calculated C2p-DOS spectrum of a benzene.
Figure 2. C K X-ray emission spectra of the pyridine-adsorbed microporous carbon system. The upper panel shows the C K X-ray emission spectra of (A) pyridine-adsorbed microporous carbon and (B) untreated microporous carbon. The lower panel shows the spectrum remaining after subtracting (B) from (A), which corresponds to the X-ray emission spectrum of adsorbate pyridine molecules in the microporous carbon. Superimposed is the calculated C2p-DOS spectrum of a pyridine molecule broadened with 0.5-eV–fwhm Lorentzian functions.

Figure 3. N K X-ray emission spectra of the pyridine-adsorbed microporous carbon system. Superimposed is the calculated N2p-DOS spectrum of a pyridine molecule broadened with 0.5-eV–fwhm Lorentzian functions.

TABLE 1: Parameters for the Cluster Models of Benzene- and Pyridine-adsorbed Microporous Carbon in DV-Xc Calculations

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a Definitions of the parameters (X_m, θ, d) are shown in Figure 4.

molecule; for example, the peak intensity ratio among the peaks a to c. These differences may be caused by the electronic interaction of the benzene molecules with the surfaces of the micropores in the microporous carbon. Therefore, they should provide information about the electronic structure and chemical bonding state of the adsorbate benzene molecules in micropores.

Figure 2 shows the C K X-ray emission spectra of the pyridine-adsorbed microporous carbon system. The upper panel shows the C K X-ray emission spectra of (A) pyridine-adsorbed microporous carbon and (B) untreated microporous carbon, which is the same spectrum as in Figure 1. The lower panel shows the spectrum remaining after subtracting (B) from (A), which should provide the X-ray spectrum of the adsorbate pyridine molecules in the microporous carbon. The subtracted X-ray spectrum (A)–(B) has a main peak at 279 eV with a high-energy shoulder near 284 eV, a low-energy shoulder near 276 eV, and a low-energy tail from 275 to 265 eV. Superimposed on it is the calculated C2p-DOS spectrum of a pyridine molecule broadened with 0.5-eV–fwhm Lorentzian functions. Major peaks in the calculated C2p-DOS spectrum are denoted by a' to g' in the figure. A comparison of the subtracted X-ray spectrum (A)–(B) with the calculated C2p-DOS spectrum shows that spectral features of the X-ray spectrum are similar to those of the calculated spectrum: the high-energy peak near 284 eV corresponds to peak a' in the calculated spectrum, the main peak at 279 eV to b', the low-energy shoulder near 276 eV to c' and d', and the low-energy tail to e' to g'. Therefore, the subtracted X-ray spectrum (A)–(B) is probably due to the adsorbate pyridine molecules. Because the size of pyridine molecule is similar to that of benzene molecule, all of the pyridine is considered to be adsorbed as a monolayer on the graphic surface of microporous carbon, as well as benzene-adsorbed system. However, its spectral features are clearly different from those in the benzene-adsorbed system, even though the same untreated microporous carbon spectrum was used for both systems. This difference is also evidence of the direct observation of adsorbate molecules in the porous microporous carbon. The fine spectral-shape differences between the X-ray spectrum of the adsorbate pyridine molecules and
the calculated spectrum may be caused by the electronic interaction of the pyridine molecules with the surfaces of the micropores in the microporous carbon.

Figure 3 shows the N K X-ray emission spectra of the pyridine-adsorbed microporous carbon. This spectrum has a main peak at 393 eV with a shoulder near 391 eV and a low-energy tail from 390 to 370 eV. Superimposed on it is the calculated N2p-DOS spectrum of a pyridine molecule broadened with 0.5-eV–fwhm Lorentzian functions. Major peaks in the calculated N2p-DOS spectrum are denoted by $a''$ to $g''$ in the figure. A comparison of the measured X-ray spectrum with the calculated N2p-DOS spectrum shows that spectral features of the X-ray spectrum are similar to those of the calculated spectrum: the high-energy peak near 393 eV corresponds to peak $a''$ and $b''$ in the calculated spectrum, the main peak at 391 eV to $c''$, and the low-energy tail to $d''$ to $g''$. Therefore, the measured X-ray spectrum is probably due to the nitrogen in the adsorbate pyridine molecules. The fine spectral-shape differences between the X-ray spectrum of the adsorbate pyridine molecules and the calculated spectrum may be caused by the electronic interaction of the lone-pair nitrogen in pyridine molecules with the micropore surface in the microporous carbon.

3.2 Configurations of Adsorbate Molecules Estimated by DV-Xα Calculations. To determine the configurations of
benzene and pyridine molecules adsorbed on the graphitic surface of microporous carbon, we compared the measured X-ray spectra with the DOS spectra of adsorbate molecules on a small graphite cluster model.

(a) Cluster Models of Adsorbate Molecules on Microporous Surface in Microporous Carbon. Cluster models of benzene- and pyridine-adsorbed on the micropore surface of the microporous carbon used in the DV-Xα calculations are shown in Table 1. The definitions of the parameters are given in Figure 4. Because the local molecular structure of microporous carbon is similar to that of graphite, as we described in the previous section, the microporous surface is modeled by graphite cluster models consisting of twenty-four carbon atoms terminated by a hydrogen atom (C_{24}H_{24}). We considered that the degree of electronic interaction between adsorbate benzene and the graphitic surface of microporous carbon may differ depending on the configuration of the adsorbed molecules, and the electronic interaction may cause spectral-shape differences. In the upper row in Figure 4, we defined the atom numberings of benzene and pyridine. Benzene has D_{6h} symmetry and pyridine has C_{3v} symmetry. The center of the aromatic rings, defined by the center of the line C_1 and C_4 in benzene and N_1 and C_3 in pyridine, was named "M". In the second row, we defined parameter X_M as the degree of parallel translation of M along the x-axis. Because the C-C bond length of benzene is 0.142 nm, we adopted a step by of half that value: 0.071 nm. In the third row, we defined θ as the rotation angle around M on the z-axis. Because the shapes of benzene and C_{24}H_{24} are equatorially hexagonal, we used only two angles: θ = 0° and 30°. For pyridine adsorbed models, we used θ = 0°, 30°, 60°, and 90° both clockwise (X_M = 0, 1 and 2) and counterclockwise (X_M = 1 and 2). In the lower row, we defined the parameter d as the distance between the benzene/pyridine aromatic rings and C_{24}H_{24}. On the basis of the fact that the distance between layers in a graphite crystal is 0.3348 nm, we used distance d = 0.16 to 0.35 nm in 0.01/0.02 nm steps for the benzene models. For the pyridine models, we used d = 0.22 to 0.34 nm in 0.02 nm steps.

To confirm the reliability of C_{24}H_{24} as a model of the surface, we calculated the C_{2p}-DOS spectra of benzene/C_{24}H_{24} and the larger adsorbed-system-model using a graphite cluster model consisting of ninety-six carbon atoms terminated by a hydrogen atom (C_{96}H_{96}). We compared the benzene-C_{2p}-DOS spectra of benzene/C_{24}H_{24} and benzene/C_{96}H_{96} and found no significant differences between them. This means the C_{24}H_{24} graphite cluster model is sufficiently large as a surface model of microporous carbon allow us to analyze the C_{2p}-DOS spectra of adsorbed states of benzene and pyridine.

We obtained the occupied benzene- and pyridine-C_{2p}-DOS spectra and pyridine-N_{2p}-DOS spectra by broadening the total C_{2p}-DOS and N_{2p}-DOS with 0.5 eV-wide Lorentzian functions. The highest-occupied-molecular-orbital (HOMO) energy was normalized at 0 eV in the molecular orbital (MO) energy.

We also carried out geometrical optimization calculations using the TINKER method to obtain a more detailed analysis of the configuration of the adsorbed molecules. The calculated models we used were some of the models used in the DV-Xα calculations transferred from the surface model (C_{24}H_{24}) to the larger graphite cluster model (C_{96}H_{96}).

(b) Benzene/C_{24}H_{24} Models. Figure 5 shows examples of the calculated occupied C_{2p}-DOS spectra of the benzene/C_{24}H_{24} models. Major peaks in this spectrum are denoted by a to g in the figure. The peaks we observed in the X-ray emission spectrum correspond to peaks a, b, and c in the C_{2p}-DOS spectrum of the benzene molecule and were well reproduced in each model. We found that the spectral-shape change mainly as a result of changing d, the distance between benzene and C_{24}H_{24}. The energy gap between peaks a and b (∆E_{a,b}) decreased from 9.0 ± 0.5 to 4.3 ± 0.1 eV as d increased from 0.16 to 0.35 nm. The energy gap between peaks a and c (∆E_{a,c}) showed the same tendency and it decreased from 6.8 ± 0.4 to 2.4 ± 0.1 eV as d increased from 0.16 to 0.35 nm. The error is the
energy gap difference caused by changing X_M or \( \theta \) by about the same \( d \); i.e., the spectral shape did not change greatly when \( X_M \) or \( \theta \) were changed. Therefore, the difference in the spectral shape was probably caused by the electronic interaction between benzene and the graphitic micropore surface of the microporous carbon that became stronger as the distance decreased. Translation along the \( x \)-axis and rotation around the \( z \)-axis has no significant effect on the difference between the spectral shapes. Thus, it is very important to estimate the distance between benzene and the graphitic micropore surface if we are to determine the configuration and electronic states of the benzene adsorbed in the microporous carbon.

First, to determine the configuration of the adsorbed states of benzene, we analyzed the distance dependence of \( \Delta E_{ab} \) and \( \Delta E_{ac} \) for all the calculated spectra, to obtain the \( d \) value that accorded best with the observed spectrum. Figure 6 shows the \( d \)-dependence of \( \Delta E_{ab} \) and \( \Delta E_{ac} \). The upper series is for \( \Delta E_{ab} \), and the lower series is for \( \Delta E_{ac} \). The upper dotted line shows the observed energy gaps of the peaks which correspond to peaks \( a \) and \( c \) (4.3 eV). The lower dotted line shows the observed energy gaps of the peaks which correspond to peaks \( a \) and \( b \) (2.4 eV). The \( d \) value that provided the best accordance between \( \Delta E_{ab} \) and \( \Delta E_{ac} \) and the observed energy gaps was about 0.33 nm. The \( \Delta E_{ab} \) and \( \Delta E_{ac} \) values for the calculated C2p-DOS spectra of unadsorbed benzene were 4.2 and 2.4 eV, respectively. Therefore, we consider the electronic states of benzene adsorbed on microporous carbon to be similar to that of unadsorbed benzene. This indicates that the adsorption mechanism of benzene on the graphitic surface of microporous carbon is physisorption. There may be no charge transfer between benzene and the graphitic surface of the micropores in the microporous carbon to create chemical connections. Figure 7 compares the observed X-ray emission spectra with the calculated C2p-DOS spectra of benzene/C_6H_{12} models at \( d = 0.33 \) nm. The observed spectra were well reproduced by our calculation models.

Next, if we wish to determine the tilt angle of the benzene aromatic ring to the graphitic surface, we cannot do so by employing an analysis of the C2p-DOS spectra obtained by DVA-Xa calculation because the spectral shapes are not sensitive to slight changes in the tilt angle of the benzene aromatic ring. So we optimized the geometry obtained with the TINKER calculations. The initial structures used in the TINKER calculations were described in the previous section. Table 2(a) shows the average distances of six carbon atoms of benzene from to C_{6H_{12}}, and the tilt angles of the benzene aromatic ring to C_{6H_{12}}. We calculated the tilt angle using \( \theta_{ring} = \arcsin \left( \frac{d_f - d_a}{0.284} \right) \); here, \( d_f \) and \( d_a \) are the distances of the farthest and nearest carbon atoms from C_{6H_{12}} surface, respectively. The diameter of the benzene aromatic ring is 0.284 nm. Benzene was most stable when it was placed with its ring almost parallel (\( \theta_{ring} = 0.0^\circ \) to 0.2\(^\circ \)) to the graphitic surface. The optimized distance from the surface is about 0.337 nm, which corresponds
well to the results obtained by DV-Xα calculation. Several studies on orientations of benzene and some hydrocarbon molecules adsorbed on a graphite crystal surface indicate that the aromatic ring of the benzene molecule is oriented parallel to the surface. Therefore, we consider that the configurations of adsorptions at the external graphite surface and at the internal graphitic surface of the microporous carbon to be similar.

(c) Pyridine/C_6H_{12} Models. Figure 8 shows examples of the calculated occupied C_{2p} and N_{2p} DOS spectra of the pyridine/C_6H_{12} models. Major peaks in the C_{2p} and N_{2p} DOS spectra are denoted in the figure by 'a' to 'g', and 'a'' to 'g'' respectively. For pyridine/C_6H_{12} parallel-models, we carried out almost the same analysis as for the benzene/C_6H_{12} models and found many similarities between them. The peaks observed in the X-ray emission spectrum, which correspond to peaks 'a' and 'b' in the C_{2p}-DOS spectrum and peaks 'a'' and 'c'' in the N_{2p}-DOS spectrum of pyridine molecule, were well reproduced in each model. The spectral-shapes differed mainly when d, the distance between the pyridine and C_6H_{12}, was changed as found with the benzene adsorption models. Moreover, there was no great change in the spectral-shape did not when X_M or X_M' were changed. Because the separation of the peaks was unclear when d was smaller than 0.30 nm, we assumed that the peak at the highest energy corresponded to 'a' and the peak with the strongest intensity corresponded to peak 'b' in the C_{2p}-DOS spectra. In the N_{2p}-DOS spectra, we also assumed that the peak at the highest energy corresponded to peak 'a'' and the peak with the second strongest intensity corresponded to peak 'c''.

The energy gap between peaks 'a' and 'b' (ΔE_α) decreased from 7.4 ± 0.4 to 4.6 ± 0.1 eV as d increased from 0.22 to 0.34 nm. The energy gap between peaks 'a'' and 'c'' (ΔE_α'') showed the same tendency and it decreased from 5.9 ± 0.3 to 3.7 ± 0.1 eV as d increased from 0.22 to 0.34 nm. The error is the energy gap difference caused by changing X_M or X_M' by about the same d, i.e., the spectral-shape did not change greatly when X_M or X_M' were changed. The results were very similar to those for the benzene models, therefore, we carried out the same analysis to determine the configurations of the pyridine adsorbed on the graphitic surface of the microporous carbon.

First, to determine the configuration of the adsorbed states of pyridine, we analyzed the distance dependence of ΔE_α and ΔE_α'' for all the calculated spectra, to obtain the d value that accorded best with the observed spectra. Figure 9 shows the d-dependence of ΔE_α and ΔE_α''. The upper panel is for ΔE_α' and the lower panel for ΔE_α'' respectively. The dotted line in the upper panel indicates the observed energy gaps of the peaks.
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Figure 9. Energy gaps, dependent on d-distance, (a) between peaks a' and b' in calculated C2p-DOS spectra and (b) between peaks a'' and b'' in calculated N2p-DOS spectra of pyridine/C_{60}H_{12} models. Measured energy gaps (4.9 eV for \( \Delta E_{\text{a'-'b'}} \) and 2.7 eV for \( \Delta E_{\text{a''-'b''}} \)) are shown by broken lines.

which correspond to peaks a' and b' (4.9 eV). The dotted line in the lower panel shows the observed energy gaps of the peaks which correspond to peaks a'' and c'' (2.7 eV). The d value at which \( \Delta E_{\text{a'}} \) and \( \Delta E_{\text{c''}} \) accord the best with the observed energy gaps was between 0.30 and 0.34 nm in the C2p-DOS spectra. The \( \Delta E_{\text{a-c}} \) value for the calculated C2p-DOS spectrum of unadsorbed pyridine was 3.2 eV. Therefore, we consider the electronic states of pyridine adsorbed on microporous carbon to be similar to that of unadsorbed pyridine. This indicates that the adsorption mechanism of pyridine on the graphitic surface of microporous carbon is physisorption as with benzene. There may be no charge transfer between the carbon atoms of pyridine and the graphitic surface of the micropores in the microporous carbon to create chemical connections.

The energy gap of the calculated N2p-DOS spectra did not accord well with that of the observed spectrum. The \( \Delta E_{\text{a-c}} \) value of the calculated N2p-DOS spectrum of the unadsorbed pyridine was 3.8 eV and this is larger than the observed energy gap (2.7 eV). Thus, we cannot find a d value that gives a smaller energy gap than 3.8 eV in our models, even if we give d an infinite value. We need N K emission spectra that have more suitable S/N ratios for further analysis.

Figure 10 compares the observed X-ray emission spectra with the calculated C2p- and N2p-DOS spectra of the pyridine/C_{60}H_{12} models at d = 0.32 nm. The observed C K emission spectrum was well reproduced by our calculation models. The calculated energy gaps \( \Delta E_{\text{a-c}} \) were about 1.0 eV larger than that of the observed N K emission spectrum, although the spectral features of the peaks in the observed spectrum were well reproduced.

Next, to determine the tilt angle of the pyridine aromatic ring to the graphitic surface of microporous carbon, we optimized the geometry obtained with the TINKER calculations. The initial structures used in the TINKER calculation were some of the models that we used in the DV-Xa calculation, except with a larger graphite cluster (C_{60}H_{32}) as a surface model. Table 2(b) shows the average distances of five carbon atoms and the nitrogen atom of pyridine from C_{60}H_{32}, and the tilt angles of the pyridine aromatic ring to C_{60}H_{32}. We calculated the tilt angle in the same way as for the benzene model. Pyridine was most stable when it was positioned with its ring slightly tilted (\( \theta_{\text{rot}} = 1.1^\circ \) to \( 1.2^\circ \)) to the graphitic surface. The optimized average distance of pyridine from the surface was about 0.338 nm, which corresponds well with the results obtained by DV-Xa calculation. The distance of the nitrogen atom was about 0.342 nm and was the furthest atom in the pyridine. This shows that the
larger tilt angle than that of the benzene model may be caused by the repulsion between the negative charge on the nitrogen atom and the π-electron of the graphitic surface. The pyridine configuration we obtained is very similar to that of another physiosorption system. A study of pyridine adsorbed on a TiO₂(110) surface indicated that pyridine was physically adsorbed on the surface. The optimized configuration of adsorbed pyridine was positioned with its ring tilted at 1.6° to the TiO₂ surface. The distance of the nitrogen, the furthest atom in the pyridine ring, to the surface, was about 0.344 nm. In another study of pyridine chemically adsorbed on such metal surfaces as Ni(100), Ag(111), Pd(111), Cu(110), and Pt(111) undertaken using theoretical and surface spectroscopic techniques, the configuration of adsorbed pyridine is shown to be tilted or almost perpendicular and lone-pair nitrogen is the nearest atom to the metal surface. This shows the great difference between the configurations of chemical adsorption on a microporous surface and physical adsorption on a graphitic microporous carbon or TiO₂ surface.

4. Conclusions

We investigated the configurations of benzene and pyridine molecules adsorbed on the graphitic surface of microporous carbon by synchrotron-radiation-excited soft X-ray emission spectroscopy and analyzed its spectral features using DV-Xa molecular orbital calculations. The main factor determining the spectral features in the C2p-DOS of the adsorbed molecules was the distance between the molecules and graphitic surface of the microporous carbon. A comparison of the C K X-ray emission spectra of the benzene- and pyridine-adsorbed systems with the C2p-DOS spectra of various adsorbed model systems showed that the distances between the molecules and graphitic surface were approximately 0.33 nm in both benzene- and pyridine-adsorbed systems. The orientations of the adsorbed molecules were both shown to be almost parallel to the graphitic surface of microporous carbon. The tilt angles were 0.0° to 0.2° for benzene and 1.0° to 1.2° for pyridine. The larger tilt angle of pyridine models may be explained by the electrostatic repulsion between the nitrogen atom and the graphitic surface. The electronic states of benzene and pyridine molecules adsorbed on the graphitic surface of microporous carbon are similar to those of nonadsorbed free molecules. We can therefore confirm that the adsorption of benzene and pyridine molecules in the microporous carbon may be physiosorption and that there may be little charge transfer between adsorbed molecules and the graphitic surface.

These results also show that synchrotron-radiation-excited soft X-ray emission spectroscopy, combined with DV-Xa molecular orbital calculations, is a powerful tool for identifying the molecular configuration and analyzing the electronic structure of adsorbates in bulk microporous materials.

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References and Notes

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