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σ-bonding contribution of a strong π-acceptor molecule: Surface chemical bond of SO_2 on Ni(100)

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We study the electronic structure and chemical bonding of the SO_2 molecule adsorbed on Ni(100) surface using x-ray emission spectroscopy at the O 1*s* absorption edge. Elemental and symmetry specificities of the method enable us to directly probe surface chemical bonding formed by strong hybridization of O 2*p* with Ni 3*d* orbital. Contrary to the expected π bonding due to strong π acceptor character of the SO_2 molecule, we find electronic structures with both σ and π characters just below the Ni Fermi level. The details of this complicated surface chemical bonding are discussed using a calculation based on density-functional theory.

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I. INTRODUCTION

Understanding the interaction between a surface and a molecule has been an important subject mainly for surface chemistry such as elementary processes of catalytic reaction and corrosion. Recently, it has also become a subject in physics because of the trend in developing organic semiconductor devices[1–3] where the interaction between a molecule and a surface metal atom serves as important fundamental knowledge in understanding functionality. However, well established photoemission spectroscopy (PES) is not convenient for observing surface-adsorbate interactions due to huge background photoelectrons from the substrate obscuring the signals from a tiny amount of adsorbates. In the late 1990s, Nilsson *et al.* applied x-ray emission spectroscopy (XES) to probe occupied electronic states for surface chemistry.[4] In XES, selective excitation of a core electron localized on a specific atom of adsorbates is followed by a radiative transition of a valence electron to the created core hole. Thus, the energy dispersion of emitted x rays reflects the element-, site-, and orbital-symmetry-specific valence electronic structures of surface adsorbates, which is free from contribution of the substrate that is not involved in the surface chemical bonding. XES reveals that actual surface chemical bond cannot be described by simple σ and π bond pictures for prototypical σ and π bonding systems, e.g., as for N_2 on Ni(100) and C_6H_6 on Ni(100).[5–8]

As another important system in investigating surface chemical bonding, we have investigated the electronic structure and chemical bonding of SO_2 adsorbed on a Ni(100) single-crystal surface by a combination of the experimental method of O 1*s* XES and density-functional theory (DFT) calculations. SO_2 molecule on Ni(100) is a characteristic system because the molecule is a stronger π acceptor than CO and gets adsorbed lying flat on the surface with partial occupancy of the π^* level of SO_2 due to charge transfer from the Ni substrate.[9] We can expect the different chemical bonding characters from CO standing up on Ni(100) and C_6H_6 lying flat on Ni(100), especially in the electronic structure around Fermi level.

II. EXPERIMENT

The experiments were performed at the C3 station of BL27SU (Refs. 10 and 11) in SPring-8. An undulator called Figure-8 enables us to selectively use horizontally and vertically polarized soft x rays. The C3 station has a high-efficiency XES spectrometer developed for surface applications.[12] Details of the whole apparatus are described in Ref. 13. A clean Ni(100) surface was prepared by repeated cycles of Ar^+ sputtering and annealing at 1000 K. The sample temperature was monitored with a thermocouple directly welded on the side of the crystal. The cleanliness of the sample substrate was checked by PES. Following the previous report,[9] multilayer and saturated-monolayer (ML) (0.4 ML) samples were prepared by dosing the clean surface with SO_2 at 50 and 170 K, respectively. To confirm the molecular orientation of the monolayer sample, we measured polarization dependent x-ray absorption spectroscopy (XAS) spectra at O 1*s* edge by Auger electron yield using an electron energy analyzer. In order to prevent radiation damage of adsorbed molecules, XES and XAS spectra were recorded with continuous scanning of the sample surface using the motorized XYZ stage.

III. RESULTS AND DISCUSSION

The inset of Fig. 1 shows polarization dependent O 1*s* XAS spectra of monolayer SO_2 on Ni(100). The O $1s \rightarrow \pi^*$ absorption (529.2 eV) is stronger when the polarization vec-

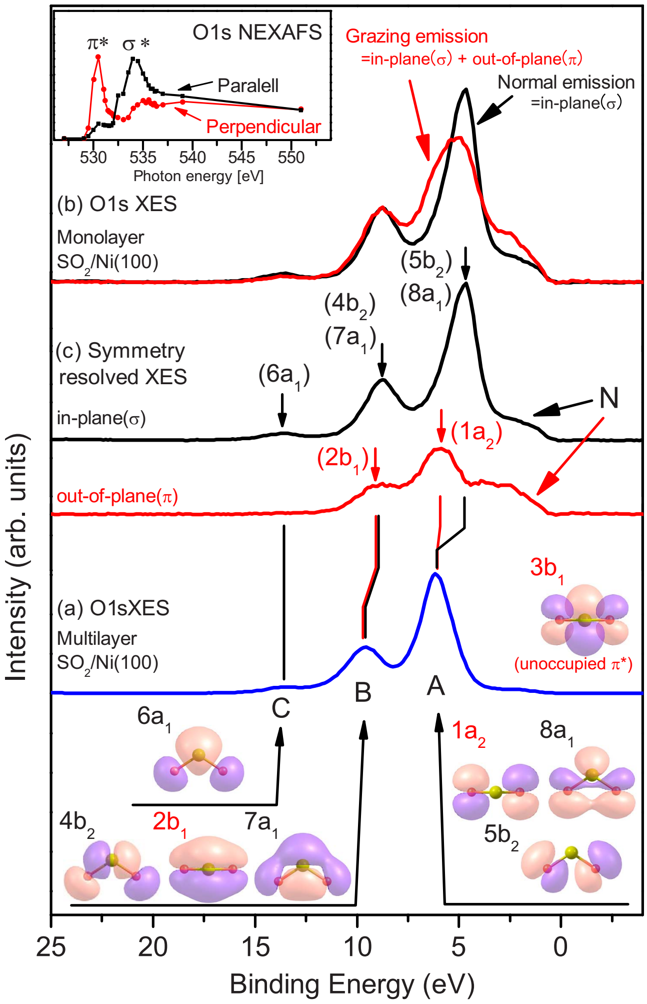

FIG. 1. (Color online) (a) O $2p \rightarrow 1s$ XES spectrum of multilayer SO_2 measured at an energy above the O $1s$ ionization threshold (540 eV). The occupied MOs corresponding to each peak and also the lowest unoccupied MO $3b_1$ (π^*) are depicted. (b) Emission angle dependence of XES spectra of saturated monolayer (0.4 ML) SO_2 on Ni(100). (c) Symmetry resolved XES spectra obtained from the spectra in (b). The elastic peak is subtracted using the spectrum obtained at excitation energy below the absorption edge. The inset shows the polarization dependence of O $1s$ XAS spectra of saturated monolayer SO_2/Ni(100).

tor of the light is perpendicular to the surface and the σ^* (533.6 eV) absorption is stronger in the parallel configuration. This result is essentially the same as reported earlier,[9] indicating that SO_2 molecule gets adsorbed lying flat on the Ni(100) surface.

Figure 1(a) shows O $1s$ XES spectrum of randomly oriented multilayer SO_2 measured above the O $1s$ ionization threshold (540 eV). The multilayer is a reference sample because the molecule does not have direct interaction with the Ni surface and intermolecular interaction by van der Waals force should be very weak. The final states of XES are one hole in valence electron states, which are basically the same as those for ultraviolet photoemission spectroscopy (UPS). A common energy scale of XES in binding energy relative to the Fermi level is obtained by subtracting the measured O $1s$ core-level photoemission binding energy from the emitted photon energies. Spectral features are very similar to those reported in UPS.[9] According to the previous UPS study, three peak structures in Fig. 1(a) can be assigned to the superposition of transitions from occupied valence molecular orbitals (MOs) with O $2p$ character to O $1s$; peak A can be assigned to $8a_1$, $1a_2$, and $5b_2$, peak B to $4b_2$, $7a_1$, and $2b_1$, and peak C to $6a_1$ orbitals, respectively.

Figure 1(b) shows resonant XES spectra of monolayer SO_2 on Ni(100) measured at O $1s \rightarrow \pi^*$ excitation. Both the normal and the grazing emission spectra relative to the molecular plane show no excitation energy dependence except for weak broadening due to multielectron excitation process, as reported in Ref. 14. This implies that the excited electron is diffused away to the substrate instantaneously and is absent in the emission process. Thus the spectra give us the direct information on the occupied electronic structure of SO_2 on Ni(100), as in the case of other adsorbed molecules reported previously.

In the monolayer spectra shown in Fig. 1(b), each MO overlapped in the multilayer spectrum is separated due to symmetry selection and chemical shift. The most remarkable difference in the spectrum between multilayer and monolayer is the appearance of a broad feature (N) near the Fermi energy (E_F) of Ni. This feature cannot be assigned in the same manner for the multilayer sample because it cannot be related directly to the valence occupied MOs of a free SO_2 molecule. We can exclude the possibility that this feature originates from decomposed fragments because there is no sign indicating the decomposition by radiation damage in both the PES and the XAS results. This characteristic feature N, which was not clearly observed in UPS study, is unambiguously originating from strong surface chemical bonding between SO_2 and Ni. Such feature was also observed in the XES spectra of N_2 and CO on Ni(100),[5,14] and was assigned to bonding MOs between the adsorbate and the surface.

Based on dipole approximation, it is possible to distinguish the symmetry of MOs observed in the normal and the grazing emission spectra of the oriented molecule in Fig. 1(b). In the normal-emission spectrum, only the emission from in-plane (σ) MOs $\rightarrow$ O $1s$ transitions is probed. On the other hand, in the grazing emission spectrum, both in-plane (σ) $\rightarrow$ O $1s$ and out-of-plane (π) $\rightarrow$ O $1s$ transitions are detected. The intensity ratio of the σ component in normal emission to that in grazing emission can be determined by simple geometrical calculus as $I_{\text{normal}}:I_{\text{grazing}}=2:1$. Then, we can deduce pure π components using the equation, $I_\pi = I_{\text{grazing}} - I_{\text{normal}}/2$. Obtained symmetry separated spectrum of π components is shown in Fig. 1(c) and is compared with that of σ components. In the spectra, some features become apparent compared to the multilayer spectrum. At least two peaks with different symmetry exist at around 5 eV while the single peak A was found in the multilayer spectrum. The peak C at 13.5 eV is observed only in the σ spectrum. In order to assign the observed symmetry selection (σ and π), simple analysis of dipole transition from occupied MOs to O $1s$ for an isolated SO_2 molecule is still useful. The MOs of $2b_1$ and $1a_2$ with π symmetry are observed at the corresponding binding energy in the out-of-plane (π) spectrum, and the MOs of $6a_1$, $4b_2$, $7a_1$, $8a_1$, and $5b_2$ with σ symmetry are observed in the in-plane (σ) spectrum, as shown in Fig. 1(c). Each electronic structure of the monolayer spectra clearly changes due to adsorption. In comparison with the XES spectrum of multilayer, the peak attributed to $5b_2$ and $8a_1$ in the σ spectrum shows large energy shift of about 1.4 eV while the peak $1a_2$ in the π spectrum shows small energy shift of about 0.3 eV. The peaks of $4b_2$ and $7a_1$ in the σ spectrum, and the peak of $2b_1$ in the π spectrum also show the energy shift of around 0.7 eV. The peak of $6a_1$ in deep level does not show noticeable energy changes. Although these peak energy shifts are related to surface chemical bonding, peak energy shift due to surface chemical bonding contains complex contributions of molecular deformation, charge transfer, etc. Therefore, further study is needed to analyze these peak shifts.

Concerning the feature N observed just below E_F of Ni in the monolayer spectra, it is expected to originate from strong hybridization between the lowest unoccupied out-of-plane MO π^* of SO_2 and the Ni $3d$ orbital, as reported on ethylene and benzene[15,16] adsorbed on Ni(100). As SO_2 is lying flat on Ni(100) surface, out-of-plane (π) MOs, which have larger overlaps between surfaces, should have strong interaction with the surface. However, in the symmetry resolved spectra in Fig. 1(c), the peak N has unexpectedly strong σ component. In case of ethylene and benzene on Ni(100), σ component is clearly weaker than π component near E_F.

In order to obtain a picture of the actual surface chemical bonding, we have performed calculations for a model cluster[17] based on the DFT (Ref. 18) using B3LYP functional.[19] Binding energies and peak intensities of the spectra were calculated by using orbital-energy differences from highest occupied MO, and transition dipole moments that were obtained by the DFT calculation. The transition dipole moments were calculated by the one-electron wave function approximately. We defined σ symmetry as corresponding to the transition dipole momentum operators being parallel to the surface and π symmetry as the transition dipole momentum operators being vertical. Since the cluster model of the surface gives discrete energy levels with ~0.7 eV spacing, it is difficult to determine the accurate origin of the binding energy, which is defined as Fermi energy in the experiment. Therefore, in this study, the two calculated spectra were simultaneously shifted by −0.5 eV to fit the experimental largest σ peak. As shown in Fig. 2(a), calculations are in good agreement with experimental XES spectra. The calculation also shows changes of MO shape due to surface-adsorbate interaction [see Fig. 2(b)]. Especially MOs corresponding to $5b_2$ and $8a_1$ show shape changes, and spreads toward the Ni atom. Concerning the electronic structure between 0–4.5 eV binding energy, the results of theoretical calculations are expanded in Fig. 3 to show the details. MOs for typical electronic states are also depicted. The theoretical calculation reveals that the peak N in Figs. 1(b) and 2(a) consists of many MOs spreading largely over surface Ni atoms; thus these MOs are corresponding to surface chemical bonding. The multiple interaction of SO_2 with more than one Ni atom due to adsorption on bridge site is the origin for the broad structure N. It is clear that σ orbitals also participate in surface chemical bonding in addition to π orbitals.

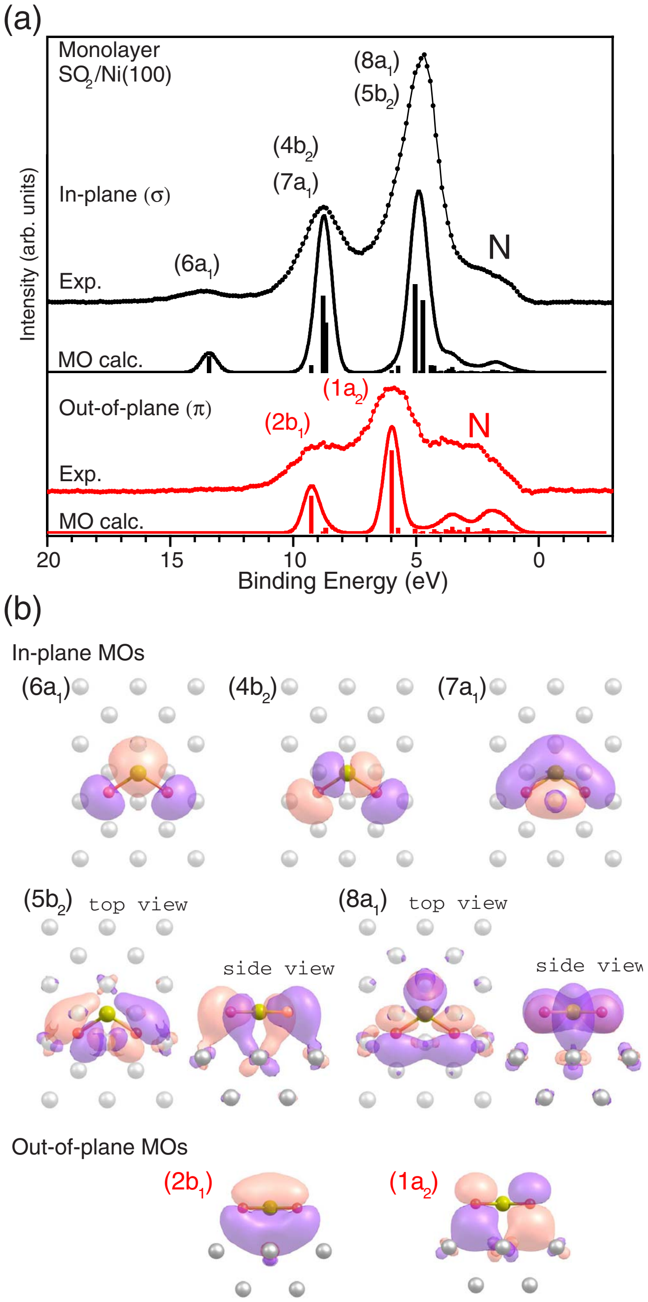

FIG. 2. (Color online) (a) Simulated XES spectra of monolayer SO_2 on Ni(100) obtained by DFT calculations together with symmetry resolved XES spectra. Simulated spectra are plotted using a convolution of the Gaussian function with the half-width at half-maximum of 0.3 eV. (b) Calculated MOs of SO_2 on Ni(100) labeled in terms of corresponding MOs of the isolated SO_2 molecule.

Which MO of SO_2 is mixing into the bonding orbitals around E_F? The shape classification of calculated MOs is able to answer the question. Contribution of unoccupied $3b_1$ (π^*) orbital, which corresponds to the charge transfer from occupied Ni $3d$ to lowest unoccupied molecular orbital of SO_2, is found in the π spectrum as 5 for example. 6 and 7 also contain the unoccupied $3b_1$ orbital (MO pictures are not shown.). As the σ spectrum, MOs 1 and 2 seem to be clearly related to $8a_1$ and $5b_2$, respectively. MOs 3 and 4 has characters from both $1a_2$ (π) and $5b_2$ (σ). The $1a_2$ character is

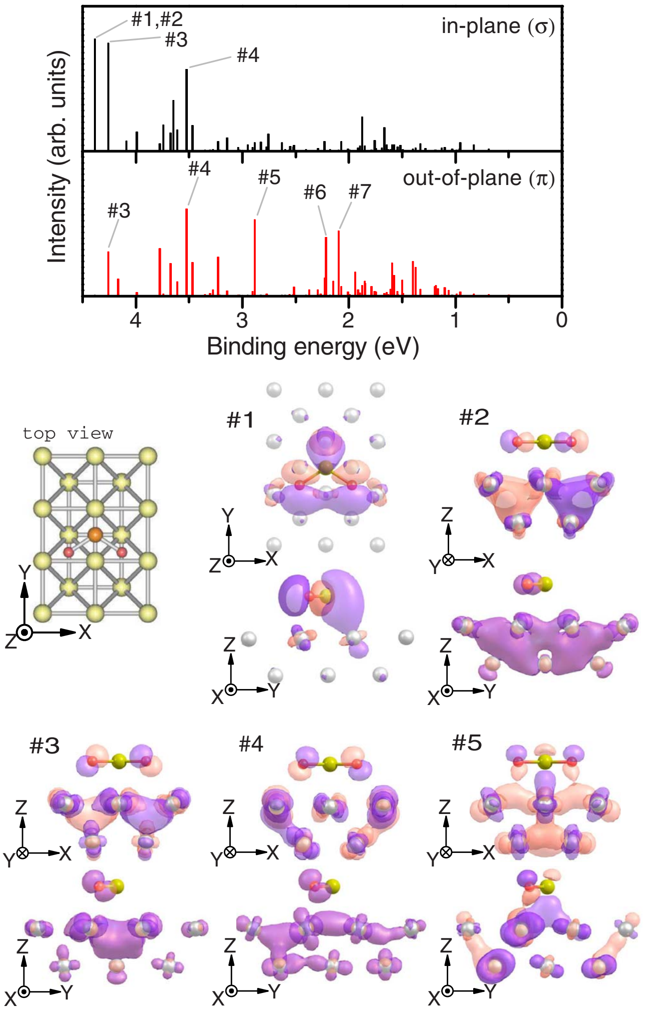

FIG. 3. (Color online) Assignment of calculated XES spectral features between 0–4.5 eV binding energy in terms of symmetry resolved π and σ states. MO pictures for typical peaks are also depicted.

stronger in 4 while the $5b_2$ character is stronger in 3. According to the experimental and the theoretical results with symmetry selection, contributions of the originally unoccupied $3b_1$ (π orbital) to surface chemical bonding were observed. In addition, the occupied MOs, $5b_2$, $8a_1$ (σ orbitals), and $1a_2$ (π orbital) also contribute to surface chemical bonding.

IV. CONCLUSION

The electronic structure and chemical bonding of SO_2 adsorbed on Ni(100) were investigated by means of O 1*s* XES and DFT calculations. The most remarkable change in adsorption is the appearance of broad features near the Fermi energy of Ni. The features are assigned to the MOs originating from strong surface chemical bonding due to strong hybridization between the O 2*p* orbitals of SO_2 and the Ni 3*d* orbital. Different from previously reported CO/Ni(100) and C_6H_6/Ni(100) systems, and contrary to the expected character of the SO_2 molecule as a strong π acceptor, our measurement shows that SO_2/Ni(100) system has characteristic chemical bonding that contains clear contribution of σ orbitals in addition to π orbitals. The observed complex behavior is associated with the adsorption structure of SO_2, lying flat on Ni(100). The combination of symmetry resolved XES and DFT calculation is an important tool to resolve complex electronic structures and surface/interface chemical bonding.

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[17] The model cluster of the Ni(100) surface consists of 18 atoms with 12 atoms in the first layer and six atoms in the second layer. The distance between Ni surface and S atom, and the angle of O-S-O were optimized by the calculations. Other geometry parameter of the Ni cluster and SO_2 molecule are fixed using the experimental value [see T. Yokoyama, S. Terada, S. Yagi, A. Imanishi, S. Takenaka, Y. Kitajima, and T. Ohta, Surf. Sci. **324**, 25 (1995)]; For Ni atoms, core electrons were represented by effective core potential of Hay-Wadt [see P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985)], and 3s, 3p, 3d, and 4s valence electrons were represented by $(5s5p5d)/(3s3p2d)$ basis functions; For S and O atoms, the cc-pVDZ basis sets [see T. H. Dunning, Jr., *ibid.* **90**, 1007 (1989)] were adopted.

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