

A theoretical study of the oxygen K-edge near-edge X-ray absorption fine structure of N₂O/Ir(110)*

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A multiple-scattering cluster method is employed to calculate the oxygen K-edge near-edge X-ray absorption fine structure of N₂O/Ir(110) and its monolayer. Two peaks and one weak resonance appear in both cases. The self-consistent field DV-X α calculations of the peaks and resonance show that the physical origin of the pre-edge peak π^* is different from those of the main peak σ_1 and the other weak resonance σ_2 . This setup is intrinsic to the N₂O monolayer, owing to the interaction between the neighbouring molecular chains in the monolayer and partly to the adsorbed atomic oxygen, according to both the theoretical and experimental data.

Keywords: N₂O/Ir(110), N₂O monolayer, multiple-scattering cluster, near-edge X-ray absorption fine structure

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1. Introduction

Nitrous oxide (N₂O) is a linear triatomic molecule in the gas phase^[1] which is best described by the ionic molecule structure $N^{-0.21}=N^{+0.49}=O^{-0.28}$.^[2] The N₂O multilayer and the interaction of N₂O with solid surfaces have been the subject of previous investigations.^[3–10] Ceballos^[3] obtained both the N and the oxygen K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra of N₂O/Cu(100), N₂O/Ag(110), and N₂O multilayers. Some weak features in the high-energy region and one strong peak in the low-energy region are present in the oxygen K-edge NEXAFS spectrum of the multilayer. The main peak is denoted as a π^* resonance. Carabineiro *et al.*^[6] investigated the adsorption of N₂O on Ir(110) at 135 K by measuring the N and oxygen K-edge X-ray absorption spectra and high-resolution resonant photoemission spectra of the system. The high-resolution resonant photoemission spectra indicate the atomic oxygen adsorbed on the surface. For the oxygen K-edge X-ray absorption spectrum, two peaks separate from 4.0 eV are observed. Comparing the oxygen K-edge spectrum in Ref. [3], Carabineiro *et al.* drew the conclusion that the main peak at 532.9 eV is related to the π^* orbitals of N₂O, and the pre-edge peak at 529.0 eV is caused by the adsorbed atomic oxygen. In our previous work,^[9] a structural model of the N₂O

monolayer has been proposed by the density functional theory.^[11–13] N₂O has a self-assembling characteristic. Thus, the oxygen K-edge NEXAFSs of both the monolayer and the N₂O monolayer of the Ir(110) system deserve further study.

The NEXAFS is a fingerprint of the local structure near an absorbing atom that contains a substantial amount of atomic and electronic structural information.^[14] However, information obtained directly from NEXAFS data seems to be limited. A theoretical analysis of the NEXAFS needs to be conducted to obtain the electronic states and geometric information. Two theoretical techniques can be employed for such an analysis. First, the dynamical theory of electron scattering in a solid is used to analyse the NEXAFS process. The multiple-scattering cluster (MSC) method is a suitable tool for studying the NEXAFS process. Second, the self-consistent field DV-X α method is used to obtain the unoccupied molecular orbitals associated with the resonances in the NEXAFS. In principle, the two above-mentioned theoretical methods should yield consistent results. Our group has successfully employed the MSC and DV-X α methods to analyse some molecular adsorption systems.^[2,4,5,8,15–20] In the present paper, MSC calculations are performed on the oxygen K-edge NEXAFS of N₂O/Ir(110) and its monolayer. The re-

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sults show a pre-edge peak x which emerges before the main peak 1 in the oxygen K-edge NEXAFS spectra. The MSC investigation reveals that the physics of the pre-edge peak x is different from that of the main peak 1.

2. MSC and DV-X α theoretical methods

NEXAFS and core-level photoelectron diffraction have similar physical origins, namely, the core-level electrons of the absorbing atom are excited by incident X-rays. The excited photoelectrons are scattered by the atoms surrounding the excited one, and they then transit into the unoccupied states of the system. The property allows the utilization of the dynamic theory of photoelectron diffraction to calculate the wave function of an intermediate photoelectron in the NEXAFS, and the absorption cross-section can be obtained by the MSC method.^[8,15]

The detailed derivation of the MSC formalism is provided elsewhere.^[15,16] Inputs to the MSC calculation include the position of atoms in the chosen cluster, the incident X-ray polarization, and the atomic phase shifts of all atoms in the cluster from which the NEXAFS can be performed. In the present paper, the atomic phase shift of each atom in N₂O and the structural parameters of the N₂O monolayer are the same as those in the literature.^[5]

A DV-X α calculation is performed for the same system to reveal the properties of the low unoccupied molecular orbitals (LUMOs) of the system associated with the resonances in NEXAFS. The DV-X α method^[21,22] is one of the most useful methods of solving the Hartree-Fock-Slater (HFS) equation based on the statistical approximation to the exchange-correlation potential. The method provides accurate electronic structures for complex systems in less computer time.^[21] Using the DV-X α method, the molecular orbitals of the system can be calculated and used to analyse the transition probability of the resonances in the NEXAFS.

3. Results and discussion

Figure 1 presents the experimental oxygen K-edge NEXAFS spectrum of N₂O/Ir(110) obtained by Carabineiro *et al.*^[6] There are two peaks (denoted as x and 1) and one weak resonance (represented as σ_1). The interval between peak 1 and the others are about

−3.9 eV (x) and 4.8 eV (σ_1). In Ref. [6], the pre-edge peak x is ascribed as the contribution from the adsorbed atomic oxygen, whereas peak 1 is attributed to the movement of 1s electrons of oxygen to the π^* orbitals of N₂O. The physical origins of these NEXAFS spectra are not clearly elucidated.

A cluster with 9 N₂O molecules and 36 Ir atoms is constructed to simulate the adsorption of the N₂O monolayer on the Ir(110) surface. The sketch map of the N₂O monolayer on the Ir(110) substrate is shown in the inset of Fig. 2. The distance between the neighbouring Ir atoms is 2.71 Å. The lengths of the edges of the N₂O monolayer are 4.07 and 3.84 Å, which are in agreement with those in Ref. [8], which are (4.1 ± 0.3) Å. The calculated spectrum is in accordance with the experimental spectrum when N₂O is set at about 3.0 Å or higher over the surface.

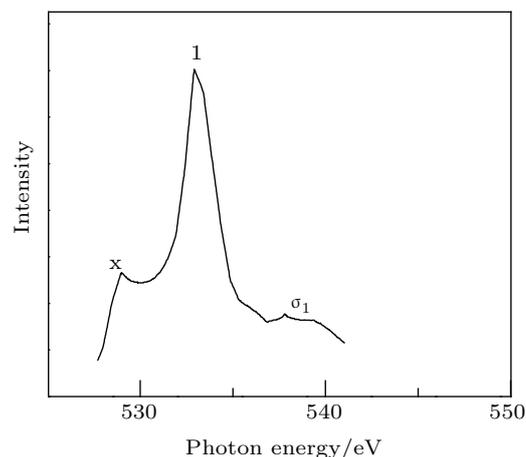


Fig. 1. Experimental oxygen K-edge NEXAFS spectrum of N₂O/Ir(110) cited from Ref. [6].

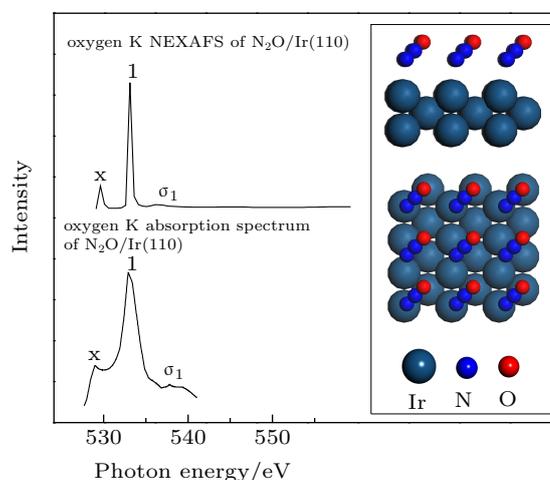


Fig. 2. (colour online) Comparison between the calculated oxygen K-edge NEXAFS spectra and the experimental data of N₂O/Ir(110). Inset is a sketch map of N₂O/Ir(110).

The calculated spectra are not dependent on the adsorption sites at such adsorption heights. The calculation results indicate that the interaction between N_2O and the Ir substrate is weak. In the calculated spectrum plotted in Fig. 2, the adsorption height of $N_2O/Ir(110)$ is taken to be 3.0 Å, and the molecule is adsorbed on the top and bridge sites.

Peaks x and 1 as well as weak resonance σ_1 appear in the oxygen K-edge calculated NEXAFS of $N_2O/Ir(110)$, and are shown in Fig. 2. The energy interval between peak 1 and the others is about -3.5 eV (x) and 3.5 eV (σ_1), which is in agreement with the experimental oxygen K-edge spectrum measured by Carabineiro *et al.*^[6] Peak x in the calculated spectrum corresponds to the pre-edge peak at 529.0 eV in the experimental spectrum. Carabineiro *et al.*^[6] considered the pre-edge peak at 529.0 eV caused by the adsorbed atomic oxygen on the surface. However, no oxygen atom was involved in the cluster chosen in the present study. The calculation spectrum indicates that the pre-edge peak is intrinsic in the oxygen K-

edge NEXAFS of the $N_2O/Ir(110)$ system and may be caused partly by the adsorbed atomic oxygen as described in Ref. [6].

Based on the above-mentioned structural parameters of $N_2O/Ir(110)$, a cluster consisting of 4 N_2O molecules and 4 Ir atoms is built to simulate the adsorption of the N_2O monolayer on the Ir(110) surface. The energy levels and orbital configuration of five LUMOs from the DV-X α calculation are listed in Table 1. LUMOs 1, 2, 3, and 4 are all π^* orbitals. Peak 1 is attributed to the transition from the O 1s core state into the four π^* orbitals. The average energy of those LUMOs is 2.42 eV above the highest occupied molecular orbital (HOMO). LUMO 5 is σ^* orbital. The weak resonance of σ_1 is attributed to the transition from the O 1s core state into the σ^* orbital. The LUMOs corresponding to peak x do not appear in the DV-X α calculation. This finding indicates that the physical origin of peak x is different from those of peak 1 and the weak resonance σ_1 .

Table 1. Energy levels and orbital configuration of $N_2O/Ir(110)$ by the DV-X α calculation.

Energy/eV	Major configuration of the orbital ^{a)}	Molecular orbital	Assigned peaks
-505.96	O (1s) 1.00	O 1s	
0	N_C (2p) 0.01, O (2p) 0.01, Ir (4f) 0.02 Ir (5d) 0.52, Ir (6s) 0.32, Ir (6p) 0.12	HOMO	
2.08	N_T (2p) 0.19, N_C (2p) 0.16, O (2p) 0.07 N_{T1} (2p) 0.14, N_{C1} (2p) 0.17, O_1 (2p) 0.09 Ir (5d) 0.04, Ir (6s) 0.03, Ir (6p) 0.11	LUMO 1 (π^*)	peak 1
2.19	N_T (2p) 0.20, N_C (2p) 0.17, O (2p) 0.07 N_{T1} (2p) 0.17, N_{C1} (2p) 0.19, O_1 (2p) 0.10 Ir (5d) 0.02, Ir (6s) 0.02, Ir (6p) 0.06	LUMO 2 (π^*)	peak 1
2.67	N_T (2p) 0.08, N_C (2p) 0.12, O (2p) 0.05 N_{T1} (2p) 0.25, N_{C1} (2p) 0.24, O_1 (2p) 0.10 Ir (5d) 0.07, Ir (6s) 0.01, Ir (6p) 0.08	LUMO 3 (π^*)	peak 1
2.72	N_T (2p) 0.14, N_C (2p) 0.17, O (2p) 0.07 N_{T1} (2p) 0.19, N_{C1} (2p) 0.19, O_1 (2p) 0.08 Ir (5d) 0.06, Ir (6s) 0.03, Ir (6p) 0.07	LUMO 4 (π^*)	peak 1
9.00	N_T (2s) 0.02, N_T (2p) 0.16, N_C (2s) 0.33 N_C (2p) 0.03, O (2s) 0.04, O (2p) 0.29 N_{T1} (2p) 0.02, N_{C1} (2s) 0.04, O_1 (2p) 0.03 Ir (6p) 0.04	LUMO 5 ($1\sigma^*$)	σ_1

^{a)} The LUMO levels with larger O (2p) components (> 0.01) are listed in the table.

A series of calculations for the oxygen K-edge NEXAFS of $N_2O/Ir(110)$ with varied adsorption heights (labeled as h) from 3.0 to 5.0 Å is performed to study the physical origin of peak x. The results are shown in Fig. 3. The calculated curves at different adsorption heights are similar, and the intensities of

peak x are almost the same.

The MSC calculation of the N_2O monolayer without substrate is also performed. The monolayer is constructed with the same structural parameters as those obtained in Ref. [9]. The sketch map of the monolayer is plotted in the inset of Fig. 4.

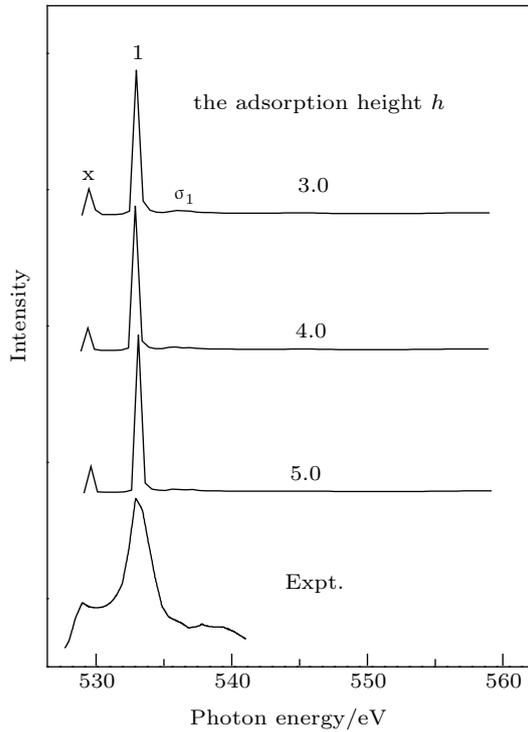


Fig. 3. Comparison between the calculated oxygen K-edge NEXAFS spectra and the experimental data of $N_2O/Ir(110)$ with adsorption height h varying from 3.0 Å to 5.0 Å.

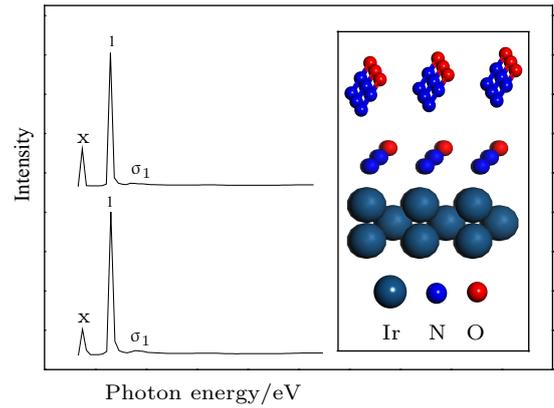


Fig. 4. (colour online) Comparison of the calculated oxygen K-edge NEXAFS spectrum between the monolayer and $N_2O/Ir(110)$. The inset shows the sketch maps of the monolayer and $N_2O/Ir(110)$.

There are two peaks (denoted as x and 1) and one weak resonance (represented as σ_1) in the calculated oxygen K-edge NEXAFS spectra of the monolayer. The interval between peak 1 and the others is about -3.5 eV (x) and 3.3 eV (σ_1). The calculated curve agrees with that of the N_2O monolayer on Ir(110). The energy levels and orbital

Table 2. Energy levels and orbital configuration of the N_2O monolayer by the DV-X α calculation.

Energy/eV	Major configuration of the orbital ^{a)}	Molecular orbital	Assigned peaks
-501.10	O (1s) 1.00	O 1s	
0	N_{T1} (2p) 0.41, N_{C1} (2p) 0.01, O_1 (2p) 0.58	HOMO	
5.61	N_T (2p) 0.19, N_C (2p) 0.17, O (2p) 0.08 N_{T1} (2p) 0.26, N_{C1} (2p) 0.20, O_1 (2p) 0.10	LUMO 1 (π^*)	peak 1
5.67	N_T (2p) 0.16, N_C (2p) 0.14, O (2p) 0.06 N_{T1} (2p) 0.29, N_{C1} (2p) 0.23, O_1 (2p) 0.12	LUMO 2 (π^*)	peak 1
6.88	N_T (2p) 0.14, N_C (2p) 0.18, O (2p) 0.07 N_{T1} (2p) 0.24, N_{C1} (2p) 0.26, O_1 (2p) 0.11	LUMO 3 (π^*)	peak 1
6.93	N_T (2p) 0.14, N_C (2p) 0.18, O (2p) 0.07 N_{T1} (2p) 0.24, N_{C1} (2p) 0.26, O_1 (2p) 0.11	LUMO 4 (π^*)	peak 1
12.98	N_T (2p) 0.04, N_C (2s) 0.08, N_C (2p) 0.01 O (2s) 0.01, O (2p) 0.07, N_{T1} (2s) 0.02 N_{T1} (2p) 0.14, N_{C1} (2s) 0.31, N_{C1} (2p) 0.03 O_1 (2s) 0.03, O_1 (2p) 0.26	LUMO 5 ($1\sigma^*$)	σ_1
13.10	N_T (2s) 0.01, N_T (2p) 0.08, N_C (2s) 0.19 N_C (2p) 0.01, O (2s) 0.02, O (2p) 0.15 N_{T1} (2s) 0.01, N_{T1} (2p) 0.09, N_{C1} (2s) 0.21 N_{C1} (2p) 0.02, O_1 (2s) 0.03, O_1 (2p) 0.18	LUMO 6 ($1\sigma^*$)	σ_1
13.20	N_T (2p) 0.03, N_C (2s) 0.06, O (2s) 0.01 O (2p) 0.05, N_{T1} (2s) 0.02, N_{T1} (2p) 0.14 N_{C1} (2s) 0.33, N_{C1} (2p) 0.03, O_1 (2s) 0.05 O_1 (2p) 0.28	LUMO 7 ($1\sigma^*$)	σ_1

^{a)}The LUMO levels with larger O (2p) components (> 0.01) are listed in the table.

configuration of the monolayer by the DV-X α calculation are listed in Table 2. LUMOs 1, 2, 3, and 4 are all π^* orbitals. Peak 1 is attributed to the transition from the O 1s core state into the four π^* orbitals. The average energy of these LUMOs is 6.52 eV above that of the HOMO. LUMOs 5, 6, and 7 are σ^* orbitals. The weak resonance of σ_1 is attributed to the transition from the O 1s core state into the three σ^* orbitals, and the average energy of these LUMOs is 13.12 eV above that of the HOMO. No LUMO corresponds to peak x in the DV-X α result. Thus, peak x does not result from the interaction between the monolayer and the Ir substrate.

A DFT study on the N₂O monolayer^[9] shows that the distance (denoted as L) between the neighbouring molecular chains is 4.1 Å. The experimental and MSC calculations of distance L varies from 3.2 Å to 4.8 Å as shown in Fig. 5. The sketch map of distance L is plotted in the inset of Fig. 5. The intensity of peak x sharply decreases with distance L increasing. Therefore, peak x is attributed to the interaction between the neighbouring molecular chains in the monolayer.

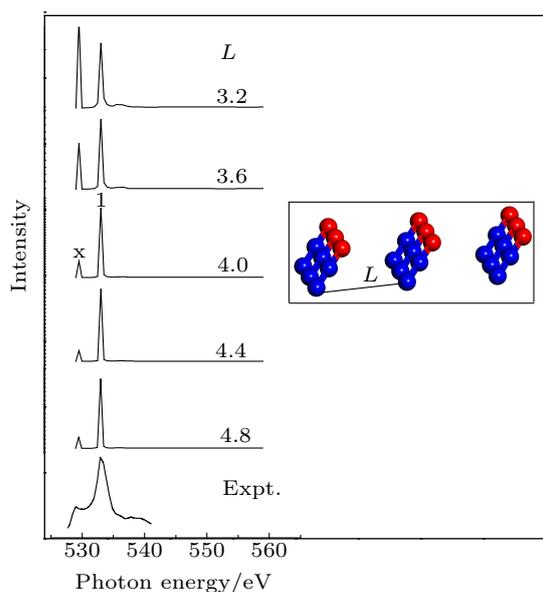


Fig. 5. (colour online) Comparison between the calculated oxygen K-edge NEXAFS spectra and the experimental data with distance L varying from 3.2 Å to 4.8 Å. The inset shows the sketch map of the monolayer.

4. Conclusion

The MSC method is employed to calculate the oxygen K-edge NEXAFS of N₂O/Ir(110) and its monolayer. The oxygen K-edge NEXAFS spectra for all cases display two peaks (denoted as x and 1) and one weak resonance (represented as σ_1). DV-X α calculations of N₂O/Ir(110) and its monolayer are performed. Peak 1 is attributed to the transition from

the O 1s core state into its π^* orbitals. The weak resonance σ_1 is ascribed to the transition from the O 1s core state into its σ^* orbitals. Peak x does not appear in the DV-X α result, so its physical origin x is different from those of peak 1 and the weak resonance σ_1 .

The MSC calculations show that peak x is dependent on the distance between neighbouring molecular chains in the N₂O monolayer but not on the adsorption height. This phenomenon is intrinsic to the oxygen K-edge NEXAFS of the N₂O/Ir(110) system and may be caused partly by the adsorbed atomic oxygen.

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