Open-boundary cluster model implemented in first-principles calculations for electronic excited states of an adsorbate-surface system

YASUI Tomokazu, NOBUSADA Katsuyuki

Physical Review B
Volume 84
Issue 245408
8-12-2011
http://id.nii.ac.jp/1146/00008218/
doi: 10.1103/PhysRevB.84.245408
Open-boundary cluster model implemented in first-principles calculations for electronic excited states of an adsorbate-surface system

Tomokazu Yasuike and Katsuyuki Nobusada*
Institute for Molecular Science and The Graduate University for Advanced Studies (SOKENDAI), Myodaiji, Okazaki, Aichi 444-8585, Japan
(Received 28 August 2011; published 8 December 2011)

Our recently developed open-boundary cluster model (OCM), which allows us to calculate electronic states of a semi-infinite adsorbate-surface system with a finite-small cluster, has been implemented in first-principles calculations to investigate excited states of a real system of a low-coverage Cs/Cu(111). The first-principles calculations are based on a real-space density functional theory (DFT) approach, and the Cs/Cu(111) system is reasonably represented in terms of a cluster of CsCu$_{13}$ within the OCM approach. An absorption spectrum and the lifetime of excited states of the system are calculated successfully within the linear-response approximation, and the computed results qualitatively agree with experimental observations. Such excited properties are difficult to calculate by using a conventional cluster model (CCM) approach. Despite these advantages, the OCM-DFT approach requires a computational cost almost identical to the cost of CCM.

DOI: 10.1103/PhysRevB.84.245408 PACS number(s): 73.20.Hb, 68.43.—h, 71.15.Qe

I. INTRODUCTION

Recently, the importance of photoexcited interfacial processes has been growing rapidly. These processes play an essential role not only in basic chemico-physical science, but also in their relevance to a broad range of practical applications to dye-sensitized solar cells, photocatalysts, artificial photosynthesis, imaging, and organic semiconductor-based photovoltaics. To investigate photoexcited interfacial systems, it is crucial to understand electronic excited states of adsorbate-metal or adsorbate-semiconductor surface systems. According to the Newns-Anderson theory, the electronic state localized on an adsorbate interacts with surface continuum states and forms a resonance state with a complex-valued eigenenergy. The imaginary part represents the decay rate of the excited state in the region near the adsorbate and corresponds physically to the irreversible electron transfer rate from the adsorbate to the substrate. The interfacial electron transfer occurring from an adsorbate excited state is a key process to determine the overall efficiency of photoexcited interfacial processes, for example, in dye-sensitized solar cells. Despite its great technological significance, fundamental understanding of the interfacial electron transfer remains unresolved. The rate of interfacial electron transfer is known to be on the order of femtoseconds for many systems. The nuclear motion cannot be a rate-determining factor in the interfacial electron transfer, unlike the electron transfer in homogeneous solutions where the nuclear reorganization process plays important roles. The electron dynamics has a direct importance, and developing a theoretical method capable of describing the resonance state in adsorbate-metal and adsorbate-semiconductor surface systems is highly desirable.

Since the conventional cluster model (CCM) and slab model approaches only give real eigenenergies, the approaches do not describe adsorbate electronic excited states interacting with metal or semiconductor surfaces appropriately. In that sense, the most reliable method at the present time is an embedded cluster model where the surface effect is described by using the surface Green function (sGF). However, this approach gives an energy-dependent effective Hamiltonian and so far, has not been used widely. Recently, we have developed the open-boundary cluster model (OCM) approach. This is a simple alternative to the embedded cluster model. A model cluster is embedded effectively by introducing the physically meaningful outgoing-wave boundary condition at the edge of the cluster. The resultant Hamiltonian is energy independent and is a good approximation to one obtained by the sGF-based embedding theory. The OCM approach also is a generalization of Nordlander-Tully’s treatment of adsorbate-jellium surfaces by using the complex-scaling technique.

The OCM approach is known to fail to describe covalent adsorptions on metal surfaces and gives a severe cluster-size dependence of computed properties whereas, it gives a good description for insulating surfaces and alkali adsorption on metal surfaces. For simple model systems, we have demonstrated that the OCM approach significantly reduces the cluster-size dependence of computed properties and has a general applicability without depending on the character of adsorption. Most noteworthy is that the OCM approach enables us to easily calculate excitation energies as well as electron-transfer rates for electronic excited states. Also, we have shown that the adsorbate excited states are decoupled from the infinite number of intrabulk excited states, and we are able to easily treat chemical reactions in photoexcited interfacial species at a low computational cost. Both potential-energy curves and electron-transfer rates for excited states are required for understanding photoexcited interfacial processes, and thus, the OCM approach is considered to be one of the most promising methods.

In the present paper, we implement our OCM approach in first-principles calculations based on the real-space density functional theory (DFT) to investigate Cs/Cu(111) as a real adsorbate-surface system. This system is ideal for the first application because a great deal of information is known about its excited states, and the adsorption has an ionic-bonding character easily treatable with a cluster model.

II. METHODS

A. DFT calculations with the OCM

The OCM Hamiltonian is constructed by introducing the outgoing-wave boundary condition (OBC) at the edge of...
where the Kohn-Sham (KS) equation \[\text{31}\] is given by
\[
\phi_i(r) = \epsilon_i \phi_i(r),
\]

where \(v(r)\), \(\rho(r)\), and \(v_{XC}(r)\) are the nuclear attraction potential, the electron density, and the exchange-correlation functional, respectively. The absorbing potential is employed to meet the outgoing boundary condition along the \(z\) direction normal to the surface so that the semi-infinity in this direction of an adsorbate-surface system is described appropriately. The explicit function form of \(v_{abs}(z)\) for \(-z_2 \leq z < -z_1\) is
\[
-v_{abs}(z) = -i \left( \frac{2\pi}{cw_{ab}} \right)^2 \left\{ \frac{2}{1 - \frac{z_1^2}{w_{ab}^2}} + \frac{2}{1 + \frac{z_1^2}{w_{ab}^2}} \right\} \cdot
\]
where \(c = 2\sqrt{\pi} \Gamma(5/4)/\Gamma(3/4)\) and \(w_{ab} = |z_2 - z_1|\). This form was proposed by Manolopoulos and co-workers\[32,33\] and was specified by a single physical parameter, the width of the absorbing region \(w_{ab}\). The value of \(-z_2\) is set to the bound of the calculation box, and \(w_{ab}\) is replaced by the scaled \(w'_{ab} = 1.125w_{ab}\) to avoid the divergence of \(v_{abs}(-z_2)\).

The orbital energies \(\epsilon_i\) become complex, \(\epsilon_i = \epsilon_i - i\gamma_i/2\), owing to the imaginary potential. The corresponding one-body density of states is given by a Lorentzian function,
\[
n_i(\epsilon) = \frac{1}{\pi} \frac{\gamma_i/2}{(\epsilon - \epsilon_i)^2 + (\gamma_i/2)^2},
\]
and the occupation number is determined by the chemical potential \(\mu\) as follows:
\[
n_i = 2 \int_{-\infty}^{\mu} n_i(\epsilon) d\epsilon = 1 - \frac{2}{\pi} \arctan \left[ \frac{2(\mu - \epsilon_i)}{\gamma_i} \right].
\]

Then, the occupation number \(n_i\) of each orbital is fractional in general. The chemical potential is more appropriate than the density should not be defined by the squared absolute values of the orbitals, \(|\psi_i(r)|^2\) but by the real parts of the squared orbitals \(\psi_i(r)^2\),
\[
\rho(r) = \sum_i n_i \text{Re}[\psi_i(r)^2].
\]
The use of the Hermite norm definition for phenomena relating to resonance\[35,36\] was criticized by Ernzerhof,\[37\] and he proposed the direct use of the complex electron density \(\sum_i |\psi_i(r)|^2\). However, the complex electron density causes severe instabilities in practical applications. According to Berggren,\[38\] the quantity on the right-hand side of Eq. (5) is interpreted as the expectation value of electron density, and it is a reasonable choice to avoid computational instability due to the variableness of exchange-correlation functional \(v_{XC}\).

\[\text{The calculations employing Eq. (5) are highly stable.}\]

\[\text{B. Excited states}\]

Excited states of adsorbate-surface systems are obtained by calculating the linear response of the ground state. The linear-response theory for a fractional-occupation number (FON) state has been formulated independently by Jørgensen\[39\] and Casida\[40\] within the frameworks of Hartree-Fock and DFT approaches, respectively. Their formulations are generalized straightforwardly for the complex-valued symmetric case by
\[
\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} \mathbf{X}^a \\ \mathbf{Y}^a \end{pmatrix} = \omega_a \begin{pmatrix} \lambda & 0 \\ 0 & -\lambda \end{pmatrix} \begin{pmatrix} \mathbf{X}^a \\ \mathbf{Y}^a \end{pmatrix},
\]
where \(\mathbf{X}^a\) and \(\mathbf{Y}^a\) vectors are formed by collecting the amplitudes for particle-hole (\(p-h\)) and hole-particle (\(h-p\)) pair excitations, respectively, in the KS orbital representation. The matrix elements of \(A, B, \lambda\) are
\[
A_{ia,jb} = (n_i - n_a)(\epsilon_a - \text{Re}(\epsilon_i)) \delta_{ij} \delta_{ab} + (n_i - n_a)(n_j - n_b)K_{ia,jb},
\]
\[
B_{ia,jb} = (n_i - n_a)(n_j - n_b)K_{ia,jb},
\]
\[
\lambda_{ia,jb} = (n_i - n_a)(n_j - n_b)\delta_{ij} \delta_{ab}.
\]
The orbital energies \(\epsilon_i\) are adopted for defining Eq. (7) because the dissipation from the occupied orbital should be canceled by the backward electron transfer in the equilibrium, i.e., the ground state.\[19\]

From the specific form of the working equation given by Eq. (6), the orthonormality relation between eigenvectors is given by
\[
\sum_{ia} (\mathbf{X}_{ia}^{a} \mathbf{X}_{ia}^{m} - \mathbf{Y}_{ia}^{a} \mathbf{Y}_{ia}^{m}) = \delta_{a,m}.
\]
The electric transition dipole moment $\mu_{0n}$ of the excitation from $|\Psi_0\rangle$ to $|\Psi_n\rangle$ is obtained by

$$
\mu_{0n} = \langle \Psi_0 | \hat{\mu} | \Psi_n \rangle = \sum_{ia} \sqrt{2} \left( X_{ia}^n \mu_{ia} + Y_{ia}^n \mu_{ia} \right),
$$

where $\hat{\mu} \equiv -\mathbf{r}$ and $\mu_{ia} \equiv \int \phi_i^*(\mathbf{r}) \hat{\mu} \phi_a(\mathbf{r}) d\mathbf{r}$. The quantity $\mu_{ia}$ is the transition dipole moment for the individual excitation of $\phi_i \rightarrow \phi_a$. The round bracket indicates the $c$ product, and the real part of $\mu_{0n}$ is the expectation value of the transition dipole moment.

C. Computational details

To investigate excited states of a Cs/Cu(111) system, we carry out the first-principles OCM calculations of CsCu$_n$ ($n = 1, 7, 10, 13, 19,$ and $31$). In these models, the substrate Cu$_n$ clusters are sections of the ideal Cu(111) surface where the Cu-Cu and interlayer distances are $2.553$ and $2.084$ Å, respectively. The adsorption of the Cs atom is known to occur on the on-top site for the Cu(111) surface at the coverage of $\frac{1}{2}$.

A. Optimization of absorbing potential

We concentrated on the low-lying excited states where only one parameter, the absorbing width $w_{ab}$, is easy to optimize. For some clusters, the self-consistent field (SCF) calculations showed a poor convergence, and thus, the Anderson mixing method was employed for the absorbing potential employed in the present paper only has one parameter, the absorbing width $w_{ab}$, it is easy to optimize the potential without ambiguity.

B. Cluster-size dependence

The intensive studies by Bagus and co-workers have shown that the CCM approach gives a reasonable description of the ground-state properties for ionic adsorption of alkali metals on transition-metal surfaces if the substrate is modeled by a cluster with an appropriate size. We first checked the cluster-size dependence of the calculated properties. Figure 2(a) is the cluster-size dependence of the ground-state Cu clusters. The overall behavior is similar between the results obtained by the CCM and OCM approaches. The OCM result is almost converged at $n \geq 13$.
This is understood qualitatively in terms of the low-electron acceptance ability of Cu. In addition to its low-electron affinity (1.23 eV), the Cu atom has a polarizability much smaller than that of the bulk Cu. Thus, the surface-image charge in the Cu(111) surface would not be represented appropriately. For this limited acceptance ability of an electron, the ionic character in the Cs-Cu bonding is expected to be underestimated. It leads to the smaller $E_{\text{int}}$ and the larger $R_{\text{CsCu}}$. This explanation can be confirmed by analyzing the dipole moment curves. The dipole moment in the $z$ direction of the surface normal is calculated by

$$\mu_z = \sum_Z Z_A \phi_z - \sum_i \phi_i(r) (-e z_i) dr,$$  \hspace{1cm} (14)

where $Z_A$ is the nuclear charge and $z_A$ and $z_i$ are the $z$ coordinates of the nucleus and the electron, respectively.

FIG. 3. (Color online) Adsorption-distance ($R_{\text{CsCu}}$) dependences of the electric dipole moment of (a) CsCu and (b) CsCu$_{13}$. The blue-dotted line is tangent to the dipole moment curve (red) at the equilibrium adsorption distance. Its slope is an index for ionicity in the adsorption bond. The actual slope values are $-0.13$ and $+1.02$ for CsCu and CsCu$_{13}$, respectively. These values imply that the Cs atom is neutral in CsCu and is cationic in CsCu$_{13}$. The CsCu$_{13}$ cluster is more appropriate for mimicking purely cationic Cs atoms in the low-coverage limit of Cs/Cu(111).
concluded that CsCu$_{13}$ is the minimal model for representing the low-coverage limit of the Cs/Cu(111) system.

The above analysis of the adsorption character explains the reason for the equilibrium adsorption distance of CsCu$_{13}$ (2.22 Å) being much smaller than the experimental value (3.01 Å). This is because the experimental value was determined under the high-coverage (0.25-ML) condition with the $p(2 \times 2)$ structure, whereas, the cluster model represents the system at the low-coverage limit. For alkali adsorbates on transition-metal surfaces, the bonding nature is known to depend on the coverage. Under the low-coverage condition, the bond is purely ionic, and it becomes covalent with increasing the coverage. With the full coverage, the Cs layer finally becomes metallic and shows a plasmonic response. Then, under the high-coverage experimental condition, the adsorption is covalent, and the adsorption distance is different from that of the ionic adsorption at the low-coverage limit. In this sense, the covalent CsCu diatomic molecule partially represents the high-coverage situation, and it is reasonable that the CsCu adsorption distance of 2.66 Å is closer to the experimental value of 3.01 Å. This is understood intuitively because the ratio of the adsorbate and substrate atoms in CsCu is higher than in CsCu$_{13}$.

### D. Previous assignment and computed photoabsorption spectrum of CsCu

The excited states of the Cu(111) and Cs/Cu(111) systems have been investigated intensively. For the clean Cu(111) surface, it has been revealed by the two-photon photoemission (2PPE) and inverse photoemission (IPE) spectroscopies that there is an excited state at around 4.1 eV. The resonant enhancement of the second-harmonic generation for the photon energy, which is half of 4.1 eV, has been reported by Lüpke et al. The electronic lifetime of this state has been determined as 10 ± 3 fs by the time-resolved 2PPE spectroscopy. This state is known to be formed by the excitation from the surface state to the image-potential state with the quantum number of $n = 1$. Due to the Cs adsorption, Cs-induced peaks arise. The lowest one is at ~ 3.0 eV for the low-coverage limit. This state was widely thought to be the Cs 6s resonance, whereas, the possibility of the Cs 5d contribution was pointed out by Arena et al. The experimentally observed lifetimes of this state are 15 ± 6 fs (Ref. 52) and 50 fs, depending on temperature. These main features of the excited states of Cs/Cu(111) and Cs/Cu(111) are summarized in Table I.

Theoretically, Borisov et al. have estimated the lifetime to be 28 fs for the lowest $\sigma$ state of Cs/Cu(111) by using a one-dimensional model potential for Cu(111). In their treatment of electron-surface interaction, only the modulation of the potential along the surface normal was considered, and a free-electron motion parallel to the surface was assumed. Their treatment is similar to the diatomic CsCu model in the sense that no Cu atoms around the Cs-adsorbed Cu atom were taken into account.

Figure 4(a) shows the computed photoabsorption spectra of CsCu in the framework of the OCM. The spectrum has four sharp peaks, indicated by A, B, C, and D, in the energy region from 2.6 to 4.2 eV. The inset shows the orbitals relevant to the excitations of A and B. Excitations A and B are mainly expressed as the excitation from the $\psi_{\text{occ}} \rightarrow \psi_a$ and $\psi_{\text{occ}} \rightarrow \psi_b$, respectively. As clearly shown by the orbital shapes of $\psi_{\text{occ}}$ and $\psi_a$, the lowest state A is attributed to the excitation from the substrate to Cs 6sp orbitals. This assignment is the same as the previous ones by Borisov and co-workers and by Nordlander and Tully. However, its excitation energy of 2.56 eV is rather lower than 3.0 eV of the experimental Cs-derived peak, and it includes no contribution from Cs 5d. On the other hand, the B state has the excitation energy of 2.95 eV close to the experimental one and is characterized mainly by Cs 5d$\sigma$. However, the absorption strength is too weak to explain the experimental IPE spectrum. Furthermore, the experimental spectrum only shows two sharp peaks in the energy region shown in Fig. 4, and the overall feature of the CsCu spectrum does not correspond to the experiment. We then conclude that the Cu atoms around the Cs-adsorbed Cu atom are needed for reproducing the photoabsorption spectrum.

### E. Photoabsorption spectra of CsCu$_{13}$

Figure 4(b) shows the photoabsorption spectrum of CsCu$_{13}$. The spectrum is quite different from that of the CsCu model.

---

**Table I. Peak positions and lifetimes of Cu(111) and Cs/Cu(111) systems.**

<table>
<thead>
<tr>
<th>System</th>
<th>Peak position and lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111) Experiment</td>
<td>4.1 eV (Refs. 46–48)</td>
</tr>
<tr>
<td></td>
<td>10 ± 3 fs (Ref. 49)</td>
</tr>
<tr>
<td>CsCu$_{13}$</td>
<td>4.06 eV</td>
</tr>
<tr>
<td></td>
<td>11 fs</td>
</tr>
<tr>
<td>Cs/Cu(111) Experiment</td>
<td>~3.0 eV (Refs. 51–54)</td>
</tr>
<tr>
<td></td>
<td>50 fs (Ref. 54)</td>
</tr>
<tr>
<td></td>
<td>15 ± 6 fs (Ref. 52)</td>
</tr>
<tr>
<td>CsCu</td>
<td>2.56 eV</td>
</tr>
<tr>
<td></td>
<td>55 fs</td>
</tr>
<tr>
<td></td>
<td>2.95 eV</td>
</tr>
<tr>
<td></td>
<td>112 fs</td>
</tr>
<tr>
<td></td>
<td>3.54 eV</td>
</tr>
<tr>
<td></td>
<td>134 fs</td>
</tr>
<tr>
<td></td>
<td>4.16 eV</td>
</tr>
<tr>
<td></td>
<td>58 fs</td>
</tr>
<tr>
<td>CsCu$_{13}$</td>
<td>2.95 eV</td>
</tr>
<tr>
<td></td>
<td>42 fs</td>
</tr>
<tr>
<td></td>
<td>3.90 eV</td>
</tr>
<tr>
<td></td>
<td>20 fs</td>
</tr>
</tbody>
</table>

4 Present results.
The number of the substrate orbitals increases from CsCu, and many additional excitation peaks appear. Their energy widths are relatively broad, and these states form a continuous background as the cluster size is enlarged further. The CsCu$_{19}$ spectrum shown in Fig. 4(c) shows continuouslike features of the background and gives more quantitative agreement with the IPE spectrum by Arena et al.\(^{53}\) indicated by the red-dashed curve. However, it should be emphasized that the CsCu$_{13}$ spectrum already reproduces the qualitative feature that there are two sharp peaks at $\sim 3.0$ and $\sim 4.0$ eV apart from the broad background. Thus, CsCu$_{13}$ is regarded as the minimal model of Cs/Cu(111) even for the excited-state properties. We discuss the assignment of these sharp peaks on the basis of the results of CsCu$_{13}$. In Fig. 4(b), two sharp peaks of CsCu$_{13}$ exist at 2.95 and 3.90 eV. The lifetime of the excited state at 2.95 eV is 42 fs and is comparable to the experimental value of 50 fs by Ogawa and co-workers.\(^{54}\) Figure 5 shows the transition-density distributions (TDDs) for the excitation at 2.95 eV. The upper and lower figures are the top and side views, respectively, of the TDDs. The total TDDs are shown on the left-hand side. As the top view clearly indicates, the radial breathing motion around the Cs-Cu axis is induced by this excitation. Therefore, the present assignment is different qualitatively from those of previous papers\(^{22,55}\) where it was assigned to the Cs 6$s\sigma$ state. The difference between the present and the previous results is due to the model potential employed for the Cu(111) surface. The previous papers used a potential uniform in the radial direction, whereas, our model explicitly has six Cu atoms around the Cs-adsorbed Cu atom. The breathing mode is stabilized by the outer six Cu atoms, and this mode becomes energetically lower than the excitation related to the Cs 6$s\sigma$ orbital of $\psi_{20}$. The partial TDD indicated by PI (partial component I) of Fig. 5 mainly contributes to the total one and consists of the excitations of $\psi_5 \rightarrow \psi_{11}$ and $\psi_6 \rightarrow \psi_{12}$. As shown in Fig. 6, the orbitals $\psi_{11}$ and $\psi_{12}$ include Cs 5$d\pi$ contributions. The next largest partial TDD, indicated

![Figure 4](image)

**FIG. 4.** (Color online) Computed photoabsorption spectra of (a) CsCu, (b) CsCu$_{13}$, and (c) CsCu$_{19}$. The inset shows the occupied and two final orbitals in excitations A and B. The yellow and orange spheres are Cs and Cu atoms, respectively. The pink and blue colors show the isosurface of the orbitals. The dark (light) colors indicate 25 (10)% of the maximal absolute value.

**Excited state at 2.95 eV (CsCu$_{13}$)**

![Figure 6](image)

**FIG. 6.** (Color online) Relevant orbitals for low-lying excitations of CsCu$_{13}$. The yellow and orange spheres are Cs and Cu atoms, respectively. The pink and blue colors show the isosurface of the orbitals. The dark (light) colors indicate 25 (10)% of the maximal absolute value.
by PII (partial component II), is formed by the excitation of \( \psi_7 \rightarrow \psi_{17} \). The orbital \( \psi_{17} \) includes the Cs 5\( d \sigma \) contribution. These Cs 5\( d \) contributions are consistent with the experimental observation by Arena et al.\(^{53}\).

Figure 7(a) shows the TDDs for the excitation of CsCu\(_{13}\) at 3.90 eV. In addition to the breathing motion, the Cu interlayer oscillation contributes to this excitation. In particular, the PII TDD of CsCu\(_{13}\) resembles the PI TDD of Cu\(_{13}\) shown in Fig. 7(b). The interlayer oscillation indicated by the PI TDD of the excitation at 4.06 eV of Cu\(_{13}\) corresponds to one of the excitations from the surface state to the image potential state (\( n = 1 \)). It is concluded that Cs/Cu(111) has the adsorbate-perturbed Cu interlayer excitation at a slightly lower energy than that of the Cu(111) excitation. The experimental lifetime of the excited state at 4.1 eV of Cu(111) is 10 ± 3 fs, and the computed lifetime of the excitation at 4.06 eV of Cu\(_{13}\) is 11 fs. The agreement is excellent, and it is one of the confirmations of the validity of the present calculation.

IV. CONCLUSION

First-principles calculations combined with the OCM approach have been applied to electronic excited states of a Cs/Cu(111) adsorbate-surface system. The OCM approach allows us to reasonably model the semi-infinite Cs/Cu(111) system with a finite-small CsCu\(_{13}\) cluster. The analysis based on the dipole moment curve has revealed that the Cs adsorption is purely ionic for the low-coverage limit of Cs adsorption, whereas, the smallest cluster model of Cs/Cu inappropriately represents Cs adsorption to be a covalent bonding.

The computed photoabsorption spectrum of CsCu\(_{13}\) gives good agreement with the experimental IPE spectrum by Arena et al.\(^{53}\). The assignment of the sharp peaks at ~3.0 and 4.0 eV is carried out by analyzing the TDDs and orbitals relevant to the excitations. The analysis concludes that the lower peak has a large contribution from the radial breathing motion of the substrate electrons. This is reasonable because the lower peak is observed strongly even for very small coverage, and the intensity only depends weakly on the coverage.\(^{53}\) The present assignment is different from previous ones. The reason for that is due to the difference in surface model potentials employed in the calculations. Our cluster model considers the Cu atoms existing around the Cs-adsorbed Cu atom to reproduce a real Cs/Cu(111) system, whereas, a rather simple model potential, that is, uniform potential in the radial direction, was employed in previous papers. The computed lifetime of the state at 2.95 eV is 42 fs comparable to 50 fs observed by Ogawa et al.\(^{54}\) Moreover, the Cs 5\( d \) contribution in the computed excited state corresponds to the observation by Arena et al.\(^{53}\) The higher-energy peak has been revealed to be reminiscent of the excitation from the surface state to the image-potential state with \( n = 1 \) of Cu(111). The detailed comparison of the properties obtained by the OCM approach with the experimental evidence clearly demonstrates the validity of our approach. The OCM approach requires a computational cost similar to the cost of the CCM and is a powerful tool for discussing the photoexcited interfacial molecular processes.

ACKNOWLEDGMENTS

The research was supported by a Grant-in-Aid (Grants No. 21350018 and No. 23750028) and by the Next-Generation Supercomputer Project from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Y. Matsumoto and K. Watanabe for helpful discussions and comments regarding the electronic states of Cs/Cu(111).

---

\(^{8}\)B. A. Gregg, MRS Bull. 30, 20 (2005).
\(^{10}\)A. J. F. Siegert, Phys. Rev. 56, 750 (1939).