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Model building of metal oxide surfaces and vibronic coupling density as a reactivity index: Regioselectivity of CO adsorption on Ag-loaded GaO

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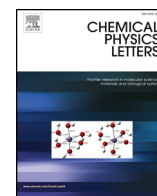
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Research paper

 Model building of metal oxide surfaces and vibronic coupling density as a reactivity index: Regioselectivity of CO<sub>2</sub> adsorption on Ag-loaded Ga<sub>2</sub>O<sub>3</sub>

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## HIGHLIGHTS

- A step-by-step hydrogen terminated cluster model of the Ga<sub>2</sub>O<sub>3</sub> surface is constructed.
- The Ag atom reacts with the Lewis basic O atom in the Ga<sub>2</sub>O<sub>3</sub> cluster.
- Vibronic coupling density identifies the adsorption site of CO<sub>2</sub> on the Ag/Ga<sub>2</sub>O<sub>3</sub>.
- Adsorbed CO<sub>2</sub> has a bent structure.

## A B S T R A C T

The step-by-step hydrogen-terminated (SSHT) model is proposed as a model for the surfaces of metal oxides. Using this model, it is found that the vibronic coupling density (VCD) can be employed as a reactivity index for surface reactions. As an example, the regioselectivity of CO<sub>2</sub> adsorption on the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> photocatalyst surface is investigated based on VCD analysis. The cluster model constructed by the SSHT approach reasonably reflects the electronic structures of the Ga<sub>2</sub>O<sub>3</sub> surface. The geometry of CO<sub>2</sub> adsorbed on the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster has a bent structure, which is favorable for its photocatalytic reduction to CO.

## 1. Introduction

Heterogeneous catalysis, particularly for reactions between molecules and solid surfaces, has been extensively studied [1]. To design heterogeneous catalysts and understand of their mechanisms, the sites for molecular adsorption on the solid catalyst must be clarified. The adsorption sites can be predicted theoretically by finding the position of a molecule on a surface that has the lowest energy of all possible positions on the surface. However, it is impractical to calculate all the energies because, in general, there are many adsorption sites for a molecule on a solid surface. Therefore, a reactivity index to predict the adsorption sites based only on the information of solid surface is desirable.

Previously, we identified the regioselectivity of cycloaddition to fullerene [2–4], metallofullerene [5], and large polycyclic aromatic hydrocarbons [6] using the vibronic coupling density (VCD) as the reactivity index. Vibronic coupling, the coupling between electron and nuclear vibrations, stabilizes a system by structural relaxation after charge transfer. The VCD as a function of a position identifies the

reactive sites as those where the vibronic coupling is large. It is expected that the VCD can be utilized as a reactivity index for systems with various reactive sites, such as solid surfaces.

$\beta$ -Ga<sub>2</sub>O<sub>3</sub> is a heterogeneous catalyst that reduces CO<sub>2</sub> to CO using H<sub>2</sub> as a reductant under photoirradiation [7,8]. The selectivity of CO<sub>2</sub> reduction is increased by modifying  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with Ag, which acts as a cocatalyst [9–13]. H<sub>2</sub>O, which is abundant, is used as the reductant in the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> system. In this study, we applied VCD to the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> surface to show the effectiveness of VCD as a reactivity index for CO<sub>2</sub> adsorption on the surface. This is the first report of the application of VCD to a solid surface and could provide the basis for extending the applicability of VCD to solid surfaces in general.

Reactivity indices, such as the frontier orbital density or VCD, strongly depend on the electronic structure of the frontier level. When building a model for the surface reactions of metal oxides based on a bulk crystal structure, the treatment of dangling bonds strongly affects the electronic structure. For instance, because hydrogen termination for dangling bonds involves electron doping, the frontier level is shifted by hydrogen termination. In this study, to build a model for the subsequent

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calculations, we employed a step-by-step hydrogen-terminated (SSHT) approach to reproduce the experimental observations.

In Section 2, we describe the theory of vibronic coupling. In Section 3, we describe the computational methods. In Section 4.1, we present a method to build a cluster model of the Ag-loaded  $\text{Ga}_2\text{O}_3$  surface by the SSHT approach. In Section 4.2, we investigate the regioselectivity of  $\text{CO}_2$  adsorption on Ag-loaded  $\text{Ga}_2\text{O}_3$  cluster using VCD as the reactivity index. Finally, in Section 5, we present the conclusions of this study.

## 2. Theory

In the early stage of chemical reactions, charge transfer occurs between reactants by intermolecular orbital interactions. Following charge transfer, the system is further stabilized by intramolecular deformation. This structural relaxation is induced by vibronic coupling. The vibronic coupling constant (VCC)  $V$ , which quantitatively evaluates the strength of vibronic couplings, is defined by [14,15]

$$V = \left( \frac{\partial E_{\text{CT}}}{\partial \xi} \right)_{\mathbf{R}_0}, \quad (1)$$

where  $E_{\text{CT}}$  is the total energy of the charge-transfer state, and  $\mathbf{R}_0$  is the equilibrium geometry before charge transfer.  $\xi$  is the reaction coordinate along the nuclear vibration that gives the largest vibronic coupling

$$\xi = \sum_{\alpha} \frac{V_{\alpha}}{\sqrt{\sum_{\alpha} |V_{\alpha}|^2}} Q_{\alpha}, \quad (2)$$

where  $Q_{\alpha}$  is a normal coordinate and  $V_{\alpha}$  is the VCC of vibrational mode  $\alpha$ .

The VCD  $\eta$  is provided by the integrand of the VCC,

$$V = \int d^3\mathbf{r} \eta(\mathbf{r}). \quad (3)$$

Since  $\eta(\mathbf{r})$  is a function of the spatial coordinate  $\mathbf{r}$ ,  $\eta(\mathbf{r})$  gives the local information about the VCC. The VCD can be divided into electronic and vibrational contributions:

$$\eta(\mathbf{r}) = \Delta\rho(\mathbf{r}) \times v(\mathbf{r}). \quad (4)$$

$\Delta\rho(\mathbf{r})$  is the electron density difference between neutral and charge-transfer states, and  $v(\mathbf{r})$  is the potential derivative defined as the derivative of the potential acting on an electron from all the nuclei  $u$  with respect to  $\xi$ . The total differential of the chemical potential  $\mu = \mu[N;u]$  which is a functional of the number of electrons  $N$  and  $u$  is given by [14]

$$d\mu = 2\zeta dN + \int \eta(\mathbf{r}) d\xi d^3\mathbf{r}, \quad (5)$$

where  $\zeta$  is the absolute hardness. In terms of the chemical reactivity theory proposed by R. G. Parr and W. Yang [16,17], the preferred direction for a reagent approaching a species is the one for which the initial  $|d\mu|$  is the maximum. The first term on the right-hand side of Eq. (5) is less direction sensitive than the second term. Thus, the preferred direction can be said to be that for which the  $\eta(\mathbf{r})$  of a species is a maximum.

## 3. Computational method

For the calculations of the VCC and VCD, we first optimized the geometry of a neutral Ag-loaded  $\text{Ga}_2\text{O}_3$  cluster and performed a vibrational analysis. Then, we calculated the forces acting on the nuclei for the neutral optimized structure in a cationic state. The charge-transfer state was chosen to be a cationic state because we assume that an electron is transferred from the Ag-loaded  $\text{Ga}_2\text{O}_3$  surface to  $\text{CO}_2$  in the reduction of  $\text{CO}_2$ . Finally, we determined the adsorbed structure of  $\text{CO}_2$  on the Ag-loaded  $\text{Ga}_2\text{O}_3$  cluster. Orbital levels were calculated with the extended Hückel theory using the geometry optimized structures by the density functional theory. The computational level was set at the

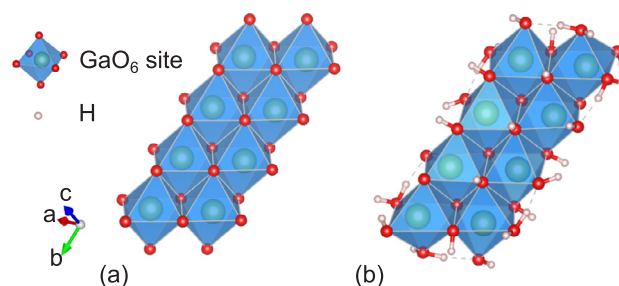


Fig. 1. Structures of the (a) bare and (b) SSHT model for the  $\text{Ga}_2\text{O}_3$  surface where Ga atoms are located at the octahedral sites formed by O atoms.

B3LYP/6-31G(d,p) level for the Ga, O, and H atoms and at the B3LYP/LANL2TZ level for the Ag atom. The core electrons in the Ag atom were replaced by effective core potentials. These calculations were performed using GAUSSIAN 09 [18,19]. The VCD analysis and extended Hückel theory calculations were performed using our own code.

## 4. Results

### 4.1. Cluster model of Ag-loaded $\text{Ga}_2\text{O}_3$ surface

$\beta\text{-Ga}_2\text{O}_3$  consists of Ga atoms located at the octahedral and tetrahedral sites formed by O atoms [20,21], as illustrated in Fig. S1 in the Supplementary Material. The octahedra share edges whereas the tetrahedra share corners in the  $b$ -axis direction. The tetrahedra also share corners with the octahedra. We expected that the electrons used for the reduction of  $\text{CO}_2$  migrate through the octahedra shared edges. In this study, eight adjacent octahedral sites are employed as a bare cluster model of the  $\beta\text{-Ga}_2\text{O}_3$  surface (Fig. 1 (a)).

Fig. 2 shows the calculated orbital levels of the bare cluster. The band gap of  $\beta\text{-Ga}_2\text{O}_3$  has been experimentally estimated to be 4.6 eV [11]. However, the energy gap of the bare cluster is 0.8 eV, which is much smaller than the experimental value. This is because the occupied molecular orbitals become unoccupied when the cluster is cut from the crystal structure. The bare cluster has reactive dangling bonds arising from the cleavage of O atoms. The dangling bonds at the O atoms are terminated by H atoms because it has been experimentally observed that H atoms are adsorbed on the  $\text{Ga}_2\text{O}_3$  surface [8]. The hydrogen termination, which involves electron doping, shifts the frontier level. The 16 unoccupied molecular orbitals must be occupied for the model to have a reasonably wide energy gap. Thus, the 32 H atoms, i.e., 2 H atoms for each unoccupied molecular orbital, are step-by-step bonded to O atoms with large molecular orbital coefficients. As a result, we

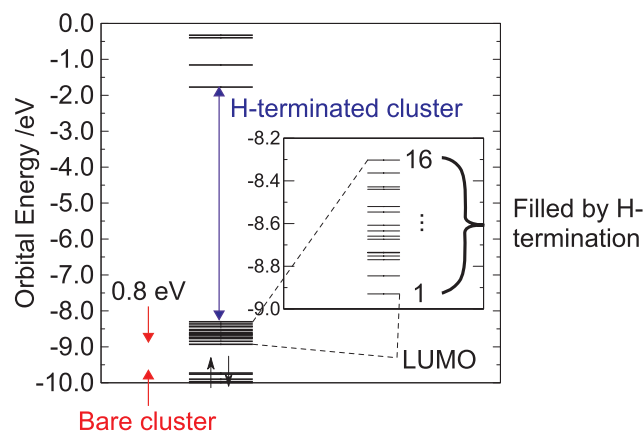
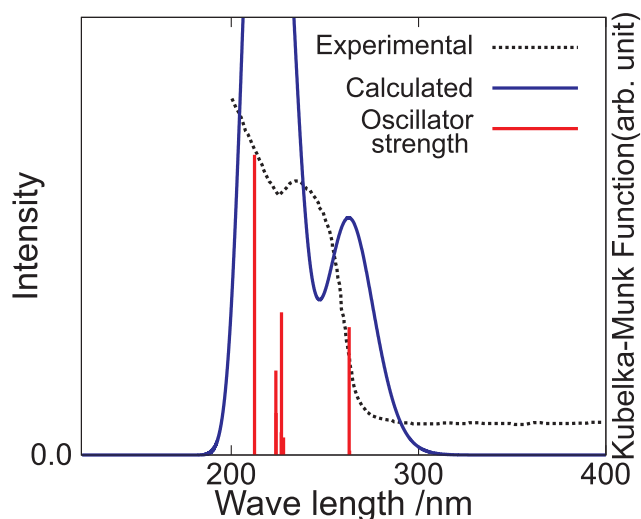


Fig. 2. Orbital levels of the bare cluster with an energy gap of 0.8 eV. Dangling bonds at the O atoms are terminated with H atoms until the cluster model has an energy gap that agrees with the experimental value.



**Fig. 3.** Experimental (black dotted line) [11] and calculated (blue line) diffuse reflectance spectra. The red lines represent calculated oscillator strengths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

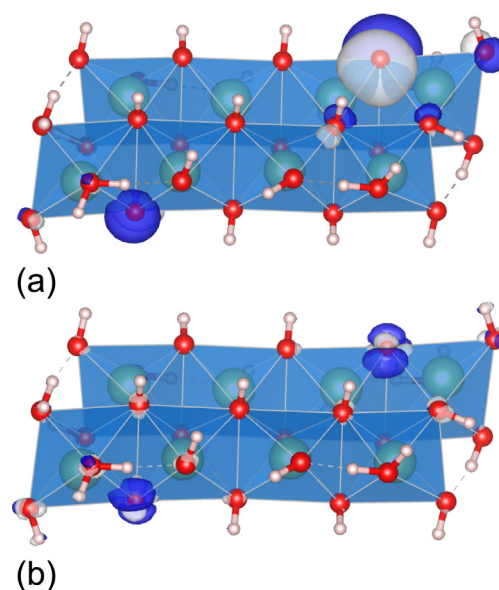
obtained the hydrogen-terminated cluster with an energy gap of 5.4 eV after geometry optimization. Fig. S2 in the Supplementary Material shows in detail the process of step-by-step hydrogen termination. Hereafter, we refer to this hydrogen terminated cluster as the SSHT model for the  $\text{Ga}_2\text{O}_3$  surface. Fig. 1 (b) shows the optimized structure of the SSHT model.

The diffuse reflectance spectrum of the SSHT cluster model is evaluated to examine its reliability. The spectrum  $g(x)$ , which depends on the absorption energy  $x$ , is calculated from the oscillator strengths multiplied by the Gaussian distribution function,

$$g(x) = \sum_{i=1}^{10} \frac{f_i}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-u_i)^2}{2\sigma^2}\right), \quad (6)$$

where  $f_i$  is the oscillator strength of a transition from  $S_0$  to the Franck–Condon  $S_i$  states, and  $u_i$  is the excitation energy from  $S_0$  to the Franck–Condon  $S_i$  states. The value of  $i$  is restricted between 1 and 10. The values of  $f_i$  and  $u_i$  were calculated using time-dependent density functional theory. Here,  $\sigma^2$  is the variance of the Gaussian distribution function and was set to  $0.05 \text{ eV}^2$ . Fig. 3 shows a comparison of the experimental and calculated diffuse reflectance spectrum [11]. Although the calculated spectrum is shifted to the long-wavelength region with respect to the experimental spectrum, the two peaks of the calculated spectrum at 219 and 263 nm are also observed experimentally. Thus, the SSHT cluster is suitable for use as a model for the  $\text{Ga}_2\text{O}_3$  surface.

It should be noted that, in the SSHT cluster model, H atoms are not bonded to all O atoms, although all the dangling bonds are terminated by H atoms. There are 20, 6, and 2 O atoms with which 1, 2, and 0 H atoms are bonded, respectively. The O atoms without hydrogen termination have a pair of electrons, and thus, act as Lewis bases. This is supported by the highest occupied molecular orbital (HOMO) of the SSHT cluster model, as shown in Fig. 4 (a), which is strongly localized on the O atoms without hydrogen termination. This result indicates that these O atoms donate electrons to the reactants. The HOMO is doubly degenerate because the Lewis basic O atoms are located at both the front and back surfaces of the SSHT cluster model. Fig. 4 (b) shows the VCD of the SSHT cluster model, which is also localized on the O atoms without hydrogen termination. The stabilization arising from the structural relaxation after charge transfer is large at the sites where the VCD is localized. Therefore, the Ag-loaded  $\text{Ga}_2\text{O}_3$  surface is modeled by placing a single Ag atom on one of the Lewis basic O atoms in the SSHT



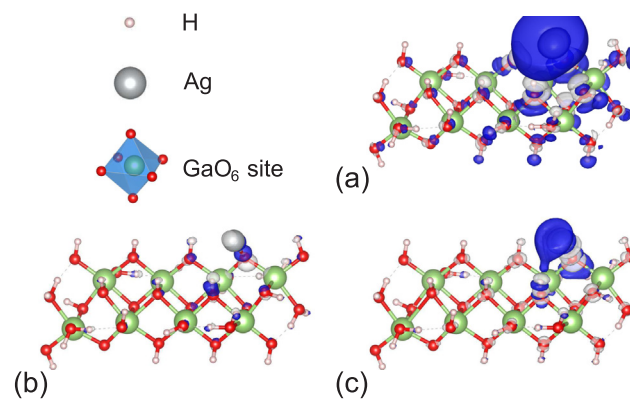
**Fig. 4.** (a) HOMO and (b) VCD  $\eta(\mathbf{r})$  of the SSHT cluster model for the  $\text{Ga}_2\text{O}_3$  surface. The HOMO and VCD are localized on the O atoms where H atoms are not bonded. The isosurface values of HOMO and VCD are  $3.0 \times 10^{-2}$  and  $2.5 \times 10^{-5}$  a.u., respectively.

cluster model. The Cartesian coordinates of the SSHT cluster model for the  $\text{Ga}_2\text{O}_3$  and Ag-loaded  $\text{Ga}_2\text{O}_3$  surfaces are given in Tables S1 and S2 of the Supplementary Material.

#### 4.2. Regioselectivity of $\text{CO}_2$ adsorption on Ag-loaded $\text{Ga}_2\text{O}_3$ cluster

Fig. 5 shows the electron density difference  $\Delta\rho(\mathbf{r})$ , the potential derivative  $v(\mathbf{r})$ , and the VCD  $\eta(\mathbf{r})$  of the Ag-loaded  $\text{Ga}_2\text{O}_3$  cluster. Here,  $\Delta\rho(\mathbf{r})$ , the electron density difference between the neutral and cationic states, is delocalized around the Ag atom because the electron is mainly extracted from the Ag atom.  $v(\mathbf{r})$  is large at the Ag and adjacent O atoms. Consequently,  $\eta(\mathbf{r})$ , which is given by the product of  $\Delta\rho(\mathbf{r})$  and  $v(\mathbf{r})$ , is localized on the Ag atom as well as on the O atoms located near the Ag atom. Since  $\eta(\mathbf{r})$  is distributed over the Ag atom and the O atoms at the surface of the  $\text{Ga}_2\text{O}_3$  cluster, structural relaxation occurs between the Ag atom and the  $\text{Ga}_2\text{O}_3$  cluster following charge transfer. This result implies that catalytic activity depends on the type of solid surface on which the Ag atom is loaded.

Geometry optimization is performed after the initial position of  $\text{CO}_2$  is set above the Ag atom, as shown in Fig. 6. The adsorbed structure of  $\text{CO}_2$  is found to have an O–C–O angle of  $139^\circ$  and O–C distances of 1.21



**Fig. 5.** (a) The electron density difference  $\Delta\rho(\mathbf{r})$ , (b) potential derivative  $v(\mathbf{r})$ , and (c) VCD  $\eta(\mathbf{r})$  of the Ag-loaded  $\text{Ga}_2\text{O}_3$  cluster. The isosurface values of  $\Delta\rho(\mathbf{r})$ ,  $v(\mathbf{r})$ , and  $\eta(\mathbf{r})$  are  $10^{-3}$ ,  $10^{-2}$ , and  $10^{-5}$  a.u., respectively.



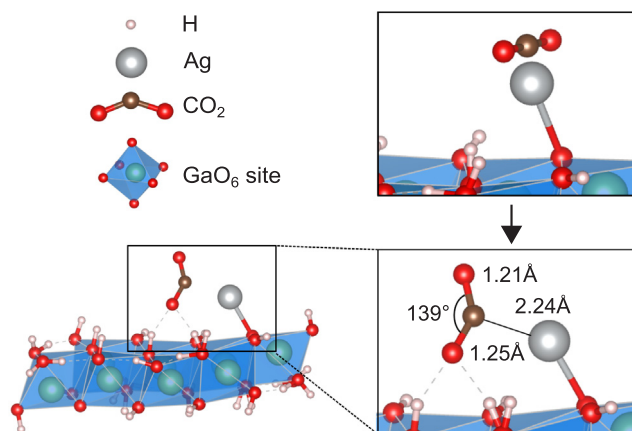


Fig. 6. Optimized structure of CO<sub>2</sub> on the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster.

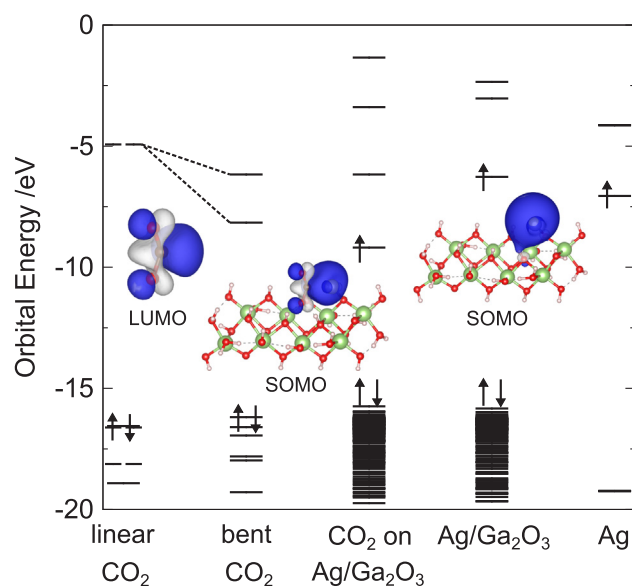


Fig. 7. Orbital levels of CO<sub>2</sub> on the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster and its fragments: CO<sub>2</sub> and Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster. Orbital levels of the linear CO<sub>2</sub> and Ag atom are also shown.

and 1.25 Å. The adsorbed structure is obtained in the region where the VCD is localized. The adsorption energy of CO<sub>2</sub>  $E_{ad}$  is defined by

$$E_{ad} = E_{CO_2} + E_{cluster} - E_{CO_2/cluster}, \quad (7)$$

where  $E_{CO_2}$ ,  $E_{cluster}$ , and  $E_{CO_2/cluster}$  are the energies of isolated CO<sub>2</sub>, isolated Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster, and CO<sub>2</sub> on the cluster, respectively. The  $E_{ad}$  of CO<sub>2</sub> is calculated to be 0.58 eV, indicating that the CO<sub>2</sub> with a bent structure is favorably adsorbed on the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster.

Fig. 7 shows the orbital levels of CO<sub>2</sub> on the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster and its fragments: CO<sub>2</sub> and Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster. Orbital levels of

the linear CO<sub>2</sub> and Ag atom are also shown. The SOMO of the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster is raised with respect to that of the Ag atom due to the interactions between the Ag atom and Ga<sub>2</sub>O<sub>3</sub>. The shift of the SOMO level of Ag is caused by the Ga<sub>2</sub>O<sub>3</sub> support. Since the SOMO of the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster is energetically close to the LUMO of the linear CO<sub>2</sub>, electron transfer occurs from the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> to the linear CO<sub>2</sub>. After the electron transfer, CO<sub>2</sub> undergoes structural relaxation from the linear structure to the bent structure. The degeneracy of LUMOs is lifted upon the structural relaxation, and the LUMO of the bent CO<sub>2</sub> is lower than the SOMO of the Ag-loaded Ga<sub>2</sub>O<sub>3</sub>. This enhances the occupation of the antibonding LUMO of CO<sub>2</sub> by photo-excited electrons transferred from photo-irradiated Ga<sub>2</sub>O<sub>3</sub>, which weakens the bond between C and O atoms. A similar orbital diagram is obtained for a Cu-loaded Ga<sub>2</sub>O<sub>3</sub> cluster model. The orbital diagrams of the Cu-loaded Ga<sub>2</sub>O<sub>3</sub> cluster and CO<sub>2</sub> are shown in Fig. S4 in the Supplementary Material. Therefore, Ga<sub>2</sub>O<sub>3</sub> loaded with a metal atom with its SOMO close to the LUMO of CO<sub>2</sub> such as Ag or Cu would be favorable for CO<sub>2</sub> reduction. In this study, the Ag and Cu are supposed to be loaded as a single atom. As shown in Fig. S5 in the Supplementary Material, the orbital diagrams of the Ag clusters exhibit a complex behavior. Therefore, the size effect of the Ag clusters would not be monotonous.

Geometry optimizations are performed by changing the initial positions of CO<sub>2</sub> to examine the dependence of the adsorbed structure. The initial positions of CO<sub>2</sub> are prepared such that CO<sub>2</sub> surrounds the Ag atom where  $\Delta\rho(\mathbf{r})$  is distributed. Although  $\Delta\rho(\mathbf{r})$  can also be used as a reactivity index, it tends to be delocalized compared to the VCD. Fig. 8 shows the optimized structures obtained for each initial CO<sub>2</sub> position. Optimized structures 1 and 2 in Fig. 8 are the same as that in Fig. 6. In structures 3 and 4, CO<sub>2</sub> has a linear structure that is unfavorable for the reduction of CO<sub>2</sub>. Furthermore, the  $E_{ad}$  of CO<sub>2</sub> for structures 3 and 4 are calculated to be 0.47 and 0.30 eV, respectively. These values are smaller than the values of  $E_{ad}$  for structures 1 and 2 of 0.58 eV. Therefore, the adsorption of CO<sub>2</sub> in the region where the VCD is localized is advantageous for the CO<sub>2</sub> reduction, as well as being the most stable of the optimized structures. Consequently, the regioselectivity of CO<sub>2</sub> adsorption is clearly indicated by the VCD because of the considerations of the vibronic contribution to the stabilization of the system in contrast to  $\Delta\rho(\mathbf{r})$ , which only considers the electronic contribution. As shown in Fig. S3 of the Supplementary Material, the optimized structures obtained by placing CO<sub>2</sub> on Ga atoms are energetically unstable compared to the structure obtained by the VCD analysis.

## 5. Conclusion

A cluster model of the Ga<sub>2</sub>O<sub>3</sub> photocatalyst surface is constructed by terminating dangling bonds with H atoms. The H atoms are bonded to O atoms with large orbital coefficients for each unoccupied orbitals such that the cluster model has an energy gap in agreement with the experimental values. The O atoms without hydrogen termination act as Lewis bases. This process of building a cluster model for metal oxide surfaces is termed as the step-by-step hydrogen-terminated (SSHT)

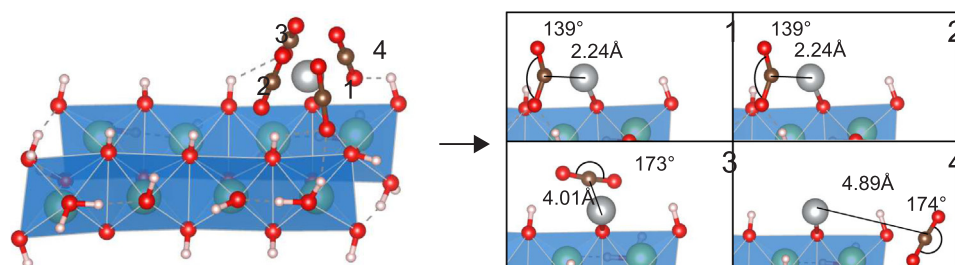


Fig. 8. Optimized structures obtained by changing the initial positions of CO<sub>2</sub> such that CO<sub>2</sub> surrounds the Ag atom.

approach. The vibronic coupling density (VCD) of the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> cluster is evaluated to identify the adsorption sites for CO<sub>2</sub>. Thus, the VCD is an effective reactivity index for determining the regioselectivity of CO<sub>2</sub> adsorption on the Ag-loaded Ga<sub>2</sub>O<sub>3</sub> surface. We also found that CO<sub>2</sub> with a bent structure, which is advantageous for photocatalytic reduction, is adsorbed on the Ag atom.

### Acknowledgments

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cplett.2018.11.036>.

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