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ABSTRACT

This study investigates the molecular and dissociative adsorption of CO and SO molecules on the perfect and a defective Ir(111) surface. It is aimed at providing a broad spectrum of adsorption sites in terms of coordination of Ir atoms and investigating the role of surface defects on the adsorption of small molecules on the surface Ir(111). First-principles density functional theory (DFT) simulation with the generalized gradient approximation as it is implemented in Vienna ab initio simulation package has been employed for this study. Preferred adsorption sites, adsorption energies, and surface electronic structures of CO and SO molecules on the perfect and defective Ir(111) surfaces were calculated to obtain a systematic understanding on the nature of adsorption and dissociative interactions. The DFT calculation reveals the possible molecular adsorption of CO on both perfect and defective Ir(111) surface by the end-on manner (CO bond perpendicular to the surface); the later surface is found to be energetically more favorable. However, no dissociative adsorption was obtained. For SO molecule, on the other hand, both molecular and dissociative adsorption was observed. The defective surface is now less favorable in terms of adsorption energy, but yields stronger activation of SO. The nudged elastic band method investigation also reveals that the Pt single-atom catalysis significantly reduces (up to 80% reduction) the energy barrier of the dissociative adsorption of SO. The electronic structure calculation reveals that all the adsorptions investigated in this study involve hybridization of different electronic states.

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I. INTRODUCTION

Attributed to both the fundamental and the applied interest, chemisorption/physisorption of small molecules on the surface of transition metals has received considerable attention. The surface–molecule interaction has been studied for potential applications in different technology and industrial processes. For instance, the interaction between transition metal surfaces and small molecules has a tendency to trigger important surface catalyzed reactions. Other applications include corrosion, lasers, and sensors. Moreover, the reconstruction of transition metal surfaces draws much attention from both researchers and technologists. While the adsorption of small molecules, such as CO, NO, O₂, and H₂, has been reported to lift the reconstruction, the adsorption of small adsorbates, such as C, N, and O, causes reconstruction. In the past, several theoretical and experimental investigations on the atomic and molecular adsorption on the transition metal surfaces have been performed. The strength of chemisorption and preference for the specific adsorption site for atomic/molecular adsorption on metal surfaces is among the main concerns of the studies in the field.

The model for chemisorption on transition metal surfaces was first proposed by Nørskov, which mainly features the importance of the position of the d-band center relative to the HOMO and LUMO of the adsorbate. Carbon monoxide (CO) as a probe molecule on transition metal surfaces is one of the most studied chemisorption systems from both experimental and theoretical points of view. Many of the studies give due attention to the geometrical properties, binding site, coverage effects, and chemisorption mechanism. The chemisorption mechanism of CO was first modeled by Blyholder in 1964, according to which the CO adsorption takes place in a linear metal –C–O structure involving the charge
transfer from CO–5σ to unoccupied metal orbitals and back donation from metal to 2π empty orbitals of CO. There are several literature studies reporting the properties of the CO adsorption on transition metal surfaces.\textsuperscript{16,17,26–28} Both dissociative and molecular adsorption of CO on metallic surfaces are observed. Previous research outputs reveal that on going from left to right and from 3d to 5d in the Periodic Table of transition metal elements, dissociative adsorption is suppressed.\textsuperscript{1,2}

The first self-consistent density functional theory (DFT) study of chemisorption on metal surfaces was reported by Ying et al.,\textsuperscript{3} which is followed by a vast number of theoretical adsorption studies of atoms/molecules on different surfaces. The increasing number of studies in this field is mainly attributed to its importance in catalysis and other applications. Despite the fact that the adsorption of small molecules on different metal surfaces, including Ni, Pb and Pt,\textsuperscript{1} has been intensively studied, less attention has been given to some of the transition metals. For instance, the adsorption of small molecules on Ir has not been sufficiently studied and its basic properties, such as adsorption structure, are not fully understood even for the most stable (111) surface. Ir shows a wide variety of potential applications as a heterogeneous catalyst in the chemical industry.\textsuperscript{1} Catalysts of both clean Ir and its alloys are used in reactions that require the activation of C–H bonds.\textsuperscript{3,4} Ir is also reported to be a potential catalyst for CO, free production of hydrogen from ammonia, production of hydrogen gas from gasoline, and selective catalytic reduction of NO,\textsuperscript{5,6} Therefore, it is worthwhile to investigate the dissociative and molecular adsorption on the surface of Ir, which might provide better understanding on the mechanism and features of molecule–Ir interactions. This study is then designed to investigate the properties and mechanism of adsorption and possible dissociation of the selected molecules on the Ir(111) surface.

As a continuation to one of our previous studies, which addresses the atomic adsorption on the Ir surface,\textsuperscript{35} we have performed theoretical investigation of functionalization of the Ir surface, this time, focusing on the dissociative and molecular adsorption. In this work, the adsorption of CO and SO molecules on the Ir(111) surface has been analyzed, where the site preference, structural parameters, and energetics of the system have been given due attention. The electronic structure interpretation has been used to provide detailed information on the molecule–surface interaction. The rest of the paper is organized as follows: details of the theoretical method are presented in Sec. II, followed by the discussion of results obtained from the DFT calculation in Sec. III, and the final section (Sec. IV) is devoted to the summary and conclusions.

II. METHOD

The interaction of the molecules with the Ir(111) surface has been investigated by means of the first-principles density functional theory (DFT) calculation as it is implemented in the Vienna\textit{ab initio} simulation package (VASP).\textsuperscript{36} The projector augmented wave (PAW)\textsuperscript{37} method and a plane wave basis set with a maximum plane-wave energy of 450 eV cutoff are used. The exchange-correlation functional is described by the Perdew–Burke–Ernzerhol (PBE)\textsuperscript{38} potential of the generalized gradient approximation (GGA).\textsuperscript{39} All parameters in the calculation are chosen to converge the total energy of 10 μeV. A 3 × 3 × 1 k-point grid is used to sample the Brillouin zone in all calculations. The substrate was represented by three layers of 5 × 5 Ir atoms for all the adsorbates included in this study. All atoms were fully relaxed except for the bottom Ir layer, which were fixed at their initial bulk-truncated positions. The C(S)O/Ir(111) adsorption was modeled by placing one C(S)O molecule onto a (5 × 5) unit cell; the molecule was placed only on one (the relaxed) side of the slab. The x and y axes were set to be parallel and the z axis perpendicular to the substrate plane. The supercell has given a dimension of 13.57 × 13.57 Å\textsuperscript{2} with periodic boundary conditions along the surface in order to represent an infinite sheet. The dimension of the supercell is believed to be large enough to avoid interactions between adatoms on periodically repeated adjacent cells. The substrate is bounded by a 20 Å dimension vacuum along the vertical direction (z axis), in order to avoid interactions between repeated slabs. The calculation has been performed for different geometrically high symmetric adsorption sites. The combined system was fully relaxed with spin polarized calculation for the initial configuration, in which the adsorbates were set to be at about 1.9 Å above the surface of the substrate. The geometry optimization of C(S)O/Ir(111) and individual components, such as the free C(S)O molecule and clean Ir(111) surface, was performed by using the conjugate gradient (CG) algorithm. The first-order Methfessel–Paxton scheme\textsuperscript{40} was used to smear the electronic states with a width of 0.1 eV.

The total energy of an isolated molecule, which is required to calculate the adsorption energies, was approximated by the calculation with a single atom in a supercell of dimension 15 × 16 × 17 Å\textsuperscript{3}. The symmetry breaking is introduced to lower the energy. The Brillouin zone in this case is sampled with only the gamma point. The DFT calculation employing the GGA is found to be quite successful in determining the bond length of the free molecule, CO. The optimized bond length obtained for the free CO molecule at equilibrium is in good agreement with an experimental value, with the error of less than 2%.

The adsorption energy of an adsorbate/molecule on the surface was calculated as

\[
\Delta E = E_{\text{total}} - E_{\text{substrate}} - E_{\text{ad}}
\]

where \(E_{\text{total}}, E_{\text{substrate}}, \) and \(E_{\text{ad}}\) are the spin polarized calculated total energies of the molecule–slab system, the pristine slab, and the isolated molecule, respectively.

III. RESULTS AND DISCUSSION

The Ir(111) surface was represented by a slab of three layers, for which the periodic boundary condition is applied laterally. The supercell is given a 5 × 5 dimension containing a total of 75 Ir atoms. The molecular adsorption was considered only on one face of the slab. The spin polarized relaxation calculation was performed for all of the atomic positions of the molecule and all the Ir atoms of the top two layers. The bottom layer of the substrate was set to be fixed for all calculations in order to model the surface properties.

The DFT calculation was performed for different possible adsorption sites. Both vertical and horizontal orientations of the molecules on the surface were taken into account. For the vertical configuration, four high symmetric adsorption sites were identified: \textit{V-top}, \textit{V-bridge}, \textit{V-fcc}, and \textit{V-hcp}. On the other hand, the horizontal
A. Ir(111)–CO system

This section of the paper presents and discusses the calculated results for the CO adsorption on the Ir(111) surface. The site preference and structural properties were investigated. The study involves both vertical and horizontal orientations of the CO molecule. Our calculation reveals that no adsorption is possible with the horizontal orientation; all the initial configurations considered in this study relaxed to structures with the vertical orientation of the CO molecule. Moreover, the O end-on configurations were repulsive for all adsorption sites. Hence, all vertical configurations mentioned hereafter refer to the C end-on (C atom facing the surface) configurations. The energetics and structural properties of the adsorption are summarized in Table I.

The adsorption configurations of CO on the Ir(111) surface, both the initial configuration and the one after adsorption, are shown in Fig. 1. For all initial configurations with vertical orientation, the CO molecule was found to be adsorbed at the corresponding site and optimized to the structure of almost the same vertical orientation. As depicted in Table I, after optimization, the CO bond distance ranges between 1.165 Å and 1.204 Å, which is longer than the bond length of the isolated CO molecule (1.15 Å). The observed bond length enlargement confirms the activation of CO on the surface. Despite the observed moderate CO bond enlargement, no dissociative adsorption was observed. The DFT calculation divulges that all the CO–surface interactions resulted in molecular adsorptions. The C–O bond elongation for each adsorption site is consistent with the downward shift of the vertical distance of the molecule above the Ir(111) surface. The adsorption strength, however, was found to follow a different approach as it increases when moving CO from fcc to bridge to hcp to top sites with vertical orientation of the molecule on the surface. Therefore, one can deduce that the C–O elongation does not follow the energetic trend.

The study reveals that the top site of the vertical orientation is the most stable adsorption site with the adsorption energy of \( -1.967 \text{ eV/CO} \). It is more stable than the bridge and three-fold hollow sites by 0.389 eV and 0.374 eV, respectively. The obtained result is in accordance with the value of PW91 and RPBE calculations. Experimental observations also proved that the top site is energetically the most favorable adsorption site for CO;\(^1,17\) the adsorption energy, however, was found to be overestimated as compared to the experimental value of about \(-1.7 \text{ eV}\).\(^{41,42}\) The adsorption of the CO molecule was thoroughly investigated for different transition metal surfaces, such as Fe, Ni, Cu, Pb, and Rh, for which the adsorption energy ranges from \(-1.28 \text{ eV}\) to \(-5.2 \text{ eV}\).\(^{43,44}\) The calculated value for the CO adsorption on the Ir surface lies within this range, implying a fairly strong chemical effect as compared to the aforementioned surfaces.

The adsorption geometry at the most stable adsorption site, V-top, provides the minimum bond length enlargement of the CO molecule and the maximum deformation of the surface as compared to that of all the other sites. This is believed to be the direct consequence of the strong binding of C to the top of an Ir atom of the surface. At this adsorption site, C is closer to one Ir atom, to which it binds, than all the other neighboring atoms. Hence, the interaction of the CO molecule is more of with this Ir atom, which leads to the highest deviation of the Ir atom from the surface with the minimal effect on the molecular structure of CO. This concept is asserted by the smallest bond length (1.848 Å) of Ir–C, the longest height \(h\) (2.111 Å) of the CO molecule from the surface, and the maximum deformation (0.263 Å) of the surface as compared to those of all the other adsorption sites.

![FIG. 1. The initial and optimized structure of CO on the Ir(111) surface. Both vertical and horizontal initial configurations with the corresponding optimized structures are presented. Suffixes 1 and 2 stand for the initial and final configurations, respectively. The red, brown, and yellow balls represent the O, C, and Ir atoms, respectively.](https://www.scitation.org/journal/adv)

| Cite     | \(\Delta E\) | \(d_{C-O}\) | \(d_{Ir-C}\) | \(h\) | \(d_{surf}\) |
|---------|-------------|---------|------------|-----|----------|
| V-hcp   | -1.593      | 1.204   | 2.125      | 1.460 | 0.072   |
| V-fcc   | -1.446      | 1.201   | 2.140      | 1.516 | 0.082   |
| V-top(H-top)\(^a\) | -1.967 | 1.165   | 1.848      | 2.111 | 0.263   |
| V-bridge(H-bridge)\(^a\) | -1.578 | 1.190   | 2.053      | 1.652 | 0.119   |
| H-hollow | -1.597      | 1.185   | 2.059      | 1.658 | 0.122   |

\(^a\)The initial configuration of H-top(bridge) was optimized to the same structure as that of the V-top(bridge) configuration.
We have also investigated the electronic structure of the CO/Ir(111) system with the purpose of providing further information on the adsorption mechanism and site preference. The projected density of states (PDOS) has been calculated for the most energetically favorable adsorption site, V-top. The PDOS for the CO molecule and the nearest Ir atom from the surface has been analyzed. The calculation has been performed both before adsorption [for the isolated CO molecule and the isolated Ir(111) surface] and after adsorption [CO/Ir(111) system] for comparison purposes. Figure 2 depicts that the density distribution for the free CO molecule is discrete. For the adsorbed CO molecule, on the other hand, the DOS distribution is found to be continuous in some specific energy levels. The continuous distribution of DOS for those particular energy levels implies the presence of a series of unoccupied states. Comparing the PDOS distribution of the free CO molecule and that of the adsorbed one reveals that there is a clear shift of states down to the lower energy levels. The sharp states observed for the free CO molecule were found to be broadened into resonance at a lower energy, implying the occurrence of electron transfer from the CO molecule to the CO/Ir system.

The DOS distribution of the d state of the closest Ir atom of the surface, as shown in Fig. 2, exhibits a significant difference between the free surface and the CO/Ir system. Between −1 eV and −4 eV and around −7 eV, a number of new DOS peaks arise compared to those on the clean Ir(111) surface. The new DOS peaks are indicators of the transfer of electrons from CO to the surface. Between −4 eV and −7 eV near the Fermi surface, the DOS of the nearest Ir atom of the CO/Ir system is found to be slightly lower than that of the clean surface. This phenomenon too can be thought to be evident for the possible electron transfer between the CO molecule and the surface. Therefore, we deduce that the CO adsorption on the Ir(111) surface is driven by hybridization of electronic states, which is also reported to be the mechanism for the adsorption of CO on the surfaces of different simple metals, including Al, Co, and Ni.1,2

Figure 2 depicts that the 5σ and 2π∗ orbitals are affected significantly due to the adsorption. The charge depletion from the CO molecule is believed to cause the reverse in the 5σ and 1π orbitals. The alteration in the 2π∗ band evidences the transfer of charges from the 5d metal band to the 2π∗ orbital of the CO molecule. This obeys the Blyholder model of CO adsorption on metallic surfaces.2

B. Ir(111)-SO system

The adsorption of the SO molecule on the Ir(111) surface has also been thoroughly investigated. Both horizontal and vertical orientations of the molecule were considered in the initial configurations, and, unlike that of the CO adsorption case, now adsorption is observed with both orientations. However, the O end-on configurations of vertical orientation were revealed to be repulsive for all adsorption sites, except at the top site, for which a weak binding with the binding energy of ~0.056 eV was observed. Therefore, the vertical configurations hereafter refer to those of the S end-on (S atom facing the surface) configurations. All the initial configurations selected to investigate the SO adsorption are similar to those used for the CO adsorption, as shown in Fig. 1. The values computed for the physical quantities of our interest in relation to the SO adsorption are summarized in Table II.

Unlike that of the CO adsorption case, the optimized structures of both vertical and horizontal orientations of the SO molecule on the surface were obtained, implying the possible adsorption of the SO molecule with both vertical and horizontal orientations on the Ir(111) surface. However, the adsorption for the later orientation is obtained to be energetically the most favorable. It is more stable by a minimum of 0.09 eV energy as compared to that of the former orientation, implying that the orientation of the SO molecule significantly impacts the adsorption.

The most stable adsorption site for the molecular adsorption is revealed to be the H-bridge site with the adsorption energy of ~2.992 eV/SO. The molecular adsorption takes place with bond length enlargement. The observed bond length enlargement is an evident implication of the SO activation on the Ir(111) surface. The adsorption geometry at the most stable molecular adsorption site, H-bridge, provides the maximum bond length enlargement as compared to that of the other molecular adsorption sites. The bond length of SO adsorbed at this site was measured to be 1.602 Å, which is too large as compared to the bond length obtained for the

![Figure 2](image.jpg)

**Figure 2.** The PDOS on the d states of the nearest Ir atom and on the s and p states of CO for the isolated case (top) and after adsorption at the V-top site (bottom).

| Cite            | ∆E   | d_{s-O} | d_{h-S} | h    | d_{surf} |
|-----------------|------|---------|---------|------|----------|
| V-hcp(V-bridge) | −2.902 | 1.471  | 2.285  | 1.699 | 0.086    |
| V-fcc           | −2.860 | 1.472  | 2.290  | 1.728 | 0.095    |
| V-top           | −0.476 | 1.482  | 2.118  | 2.322 | 0.204    |
| H-bridge(H-top) | −2.992 | 1.602  | 2.320  | 1.943 | 0.098    |
| H-hollow        | −3.706 | 3.022  | 2.289  | 1.767 | 0.180    |

*The adsorptions at the V-bridge and H-top sites were found to be unstable, yielding the same optimized structure as that at V-hcp and H-bridge sites, respectively."
isolated SO molecule 1.46 Å. This significant change in the molecular structure of SO evidences strong activation of the molecule on the Ir(111) surface. The molecular structure modification is accompanied by an appreciable amount of surface deformation ($d_{sur} = 0.098$ Å) and the second largest height ($h = 1.943$ Å), just next to that of the adsorption at the V-top site, of the molecule above the surface. The adsorption strength, in general, shows positive correlation with the enlargement of the bond length of the molecule; stronger adsorption causes a higher bond length enlargement.

In addition to the molecular adsorption, dissociative adsorption of SO on the Ir(111) surface was also observed. Among all the initially selected structures, dissociative adsorption has been observed only for one case, for which the structure includes the H-hollow adsorption site. It is interesting to notice that the dissociative adsorption is energetically more favorable than the molecular adsorption. There is a 0.714 eV energy difference between the dissociative adsorption and the most stable molecular adsorption, in favor of the former. The optimized structure for the SO adsorption at the H-hollow site (horizontal orientation of SO between successive fcc-hollow and hcp-hollow sites on the Ir(111) surface exhibits independent adsorption of S and O atoms at two successive fcc-hollow sites, Fig. 3, yielding a 3.022 Å separation between S and O. The DFT calculation of the atomic adsorption also reveals that the fcc-hollow site is the most stable adsorption site for both S and O atoms on the Ir(111) surface. Hence, the phenomenon of the dissociative adsorption of SO can be understood as both S and O atoms of the molecule start to pull apart from each other due to the respective interaction with the corresponding closest fcc-hollow sites. This, in turn, triggers the SO bond break ending up with independent adsorption of the atoms at their energetically favorable adsorption sites.

The nudged elastic band (NEB) method has been employed to investigate the transition state (TS) of the dissociative adsorption of SO for the minimum energy pathway (MEP), which was converged to the total energy accuracy of $10^{-5}$ eV. The energy barrier for the dissociative chemisorption of the SO molecule on the Ir(111) surface is found to be about $E_b = 0.6$ eV. Note that the dissociative barrier is defined as the energy difference between the initial and transition states, as shown in Fig. 4.

The observed molecular and dissociative adsorptions of SO on the Ir(111) surface were further investigated through the electronic structure computed for the most energetically favorable adsorption site; H-bridge for molecular adsorption and H-hollow for dissociative adsorption, as shown in Fig. 5. It shows that the adsorption induces a significant change in the electronic structure. The two peaks observed between $-10$ eV and $-12$ eV for non-interacting systems were found to be merged and shifted down to lower energy with higher weight after the adsorption. The adsorption also changes the density of states of the SO molecule from discrete to continuous for

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**FIG. 3.** The initial and relaxed structure of the dissociative adsorption of SO on the Ir(111) surface.

**FIG. 4.** Minimum energy pathway and energy barrier for the dissociation of SO on the Ir(111) surface. IS, TS, and FS denote the initial state, transition state, and final state, respectively. The yellow, red, and brown balls represent Ir, O, and S atoms, respectively.

**FIG. 5.** The PDOS on the d states of the nearest Ir atoms and the s and p states of the isolated and adsorbed SO molecule. The computed structures presented here are for the isolated system (top) and that interacting with adsorption at the H-bridge (middle), and at the H-hollow (bottom) sites.
some specific energy levels, implying the charge transfer for those specific energy levels. The DOS of the d states of the nearest Ir atoms shows moderate decrements after the adsorption as compared to that of the isolated case. An appreciable difference in the electronic structures was also observed between the molecular adsorption (SO adsorption at the H-bridge site) and the dissociative adsorption (SO adsorption at the H-hollow site). The two peaks mentioned above exhibit more shift to a lower energy level and less weight for the dissociative adsorption as compared to that of the molecular adsorption. Between $-8$ eV and $-4$ eV, the DOS on the d states of the nearest Ir atoms for the molecular adsorption is moderately lower than that of the dissociative adsorption.

**C. Adsorption on the defective surface**

Finally, we have investigated the impact point defects may have on the adsorption of CO and SO molecules on the Ir(111) surface. It is now a common thought that defects can drastically alter the chemistry of surfaces by lowering energy barriers and causing large changes in adsorption energies. The presence of defects consisting of certain guest atoms or holes on a surface is supposed to be capable of altering the overall interaction of the surface with adatoms/molecules. Hence, we extend this study to investigate the adsorption of CO and SO on the defective Ir(111) surface. The corresponding most stable adsorption sites, as it is discussed in Secs. III A and III B, were selected for this investigation. The point defect on the surface was taken into account by incorporating either vacuum space or a guest atom on the surface. The vacuum is formed by removing one Ir atom from the surface, whereas the guest atom replaces an Ir atom on the surface. The defect site is arbitrarily chosen on the surface, but the adsorbate was set to be near the defect site. Our investigation shows no stability problem for the defective surface. Three different guest atoms were selected for this study: Ag, Au, and Pt. The energetic and structural parameters computed for the adsorption on the defective surface are summarized in Table III.

Table III depicts that the CO adsorption is favored by the defect, which is verified by stronger binding of the molecule to the surface as compared to that of the clean surface. Both forms of defects, due to the vacuum and that of the impurity, yield stronger binding. For instance, the adsorption on the vacuum-surface is more stable than that on the clean surface by 0.136 eV energy. Similarly, the adsorption on the surface with impurity is more stable than that of the clean surface by 0.346 eV, 0.287 eV, and 0.298 eV energy, when the guest atom is Ag, Au, and Pt, respectively. The bond length enlargement also shows a slight change, for most cases it increases. The height of the adsorbed molecule above the surface significantly decreases for the vacuum-surface case, where it drops from 2.111 to 1.936. However, a much smaller change is observed in the presence of impurity. This difference is expected since the vacuum creates more space for the molecule to be closer to the surface by avoiding the repulsive interaction that would have happened with the Ir atom had the vacuum space been filled by the Ir atom.

The DFT calculation reveals that the CO adsorption on the surface doped with the Ag atom yields the most stable structure with $-2.313$ eV energy, which is the lowest of all CO adsorption cases included in this study. As compared to the one on the clean surface, the CO adsorption on the Ag doped surface is energetically favorable by 0.346 eV. The electronic structure, discussed in future paragraphs, has been computed with the purpose of elaborating the adsorption phenomenon on the Ag doped Ir(111) surface. Unlike that of the CO adsorption, the SO adsorption could not be promoted, in terms of energy, by the surface defects investigated in this study. Rather, the SO adsorption on the perfect surface was found to be energetically favorable as it can be verified by comparing the corresponding quantities in Table III with those in Table II. The most stable adsorption on the defective surface is obtained for the case of the Ag doped surface, which is at higher energy by 0.356 eV than the dissociative adsorption on the perfect surface. The hole type defect was even observed to hinder the dissociative adsorption, yielding just a molecular adsorption of the SO molecule with enlarged bond length. Despite the fact that both the molecular and dissociative adsorptions of SO on the defective surface take place at higher energy as compared to that on the perfect surface, it gives a longer SO bond length enlargement or longer separation between dissociated S and O atoms. For instance, the bond length enlargement for the molecular adsorption of SO on the defective surface (hole defect) is greater by about 2.2% than that on the perfect surface. Similarly, in the case of the dissociative adsorption, the separation between dissociated atoms was found to be increased by 15.19%, 15.25%, and 2.68% for the Pt, Au, and Ag doped surfaces, respectively, as compared to that on the perfect surface.

Moreover, the Pt atom is found to significantly reduce the energy barrier for the dissociative adsorption of SO (Fig. 6). The NEB calculation shows the energy barrier of the adsorption on the Pt doped surface to be $E_b = 0.12$ eV, which is only 20% of that on the clean surface. This should be due to the catalysis effect of the Pt atom, which can be termed single-atom catalysis. Single-atom catalysis is at the forefront of catalysis research due to its high efficiency and low cost. Pt is popular for its huge potential in the single-atom catalysis application. Our investigation reveals that the situation is totally different for other guest atoms, Ag and Au, for which the energy barrier rather increases. The obtained result suggests that even noble metals do not behave the same way as it regards to single-atom catalysis.

The computed electronic structure, as shown in Figs. 7 and 8, reveals that it is heavily affected due to the adsorption. Figure 7 depicts the shift of states down to the lower energy levels for the adsorbed CO molecule. The sharp states observed for the
free CO molecule were found to be broadened into resonance at a lower energy, indicating that electrons are transferred from the CO molecule to the Ir surface. The density distribution on the d state of the nearest Ir atoms of the oxidized Ir(111) surface is slightly lower than that of the clean surface, which evidently indicates the transfer of electrons from the surface to the CO molecule. Similarly, the DOS on the Ag atom appreciably decreases after the adsorption, suggesting that the adsorption process involves charge exchange with the guest atom too.

Figure 8 shows that the DOS of the s and p states shows a major change; the two peaks from the SO-p states near the Fermi surface and two peaks from the SO-s state around −11 eV, which were observed on the electronic structure of the isolated molecule, were found to be disappeared after the adsorption. The DOS distribution of the adsorbed SO was also found to be continuous within a certain energy range, which evidently shows a series of occupied states within that particular energy range.

IV. CONCLUSION

The molecular and dissociative adsorption of CO and SO molecules on the Ir(111) surface has been thoroughly investigated using the first-principles approach. Different configurations have been initially selected in order to establish the preferential adsorption site and the corresponding geometry. The study involves both perfect and defective surfaces with the purpose of investigating the role of surface defects in the adsorption of the molecules, in addition to providing deep understanding on the adsorption mechanism of small molecules on the Ir(111) surface. The defective surface involves a vacuum or a guest atom (Ag, Au, or Pt) replacing one Ir atom from the surface.

The molecular adsorption of CO at the top site is found to be the most stable configuration. It is adsorbed by the end-on manner, where the CO bond is perpendicular to the Ir(111) surface with the configuration of the C atom facing the surface. The adsorption involves bond enlargement, implying the CO activation on the surface. The CO adsorption at the adsorption site of preference exhibits the smallest Ir–C bond length, the longest height of the molecule above the surface, and maximum deformation of the surface as compared to that of all the other adsorption sites included in this study. The DFT calculation also reveals that the adsorption significantly changes the electronic structure of both the molecule and the surface, asserting that the adsorption involves charge transfer between the surface and the molecule. The adsorption is then believed to be driven by the hybridization of electronic states. The computed electronic structure also suggests that the CO adsorption on the Ir(111) surface owes to the Blyholder model of CO adsorption on metallic surfaces. The molecular adsorption of CO is achieved on both the perfect and defective surfaces of Ir(111); however, the latter is found...
to be energetically more favorable. All of the defects modeled in this study significantly enhance the adsorption; all the adsorptions on the defective surface take place at lower energy as compared to that on the perfect surface. Despite confirmed molecular adsorption, no dissociative adsorption was observed.

The theoretical investigation of the SO adsorption on the Ir(111) surface reveals that both molecular and dissociative adsorptions are possible. The adsorption at the H-bridge site is found to give the most stable configuration of the molecular adsorption characterized by low energy as compared to that of all the other adsorption sites. The adsorption is accompanied by bond length enlargement, implying the SO activation on the surface. It also significantly changes the electronic structure of both the molecule and the surface, suggesting that the adsorption involves hybridization of different electronic states. In addition to the molecular adsorption, dissociative adsorption of SO on the Ir(111) surface was also observed. It is found to be energetically more favorable than even the molecular adsorption; its energy is 0.714 eV lower than that of the most stable molecular adsorption. Both molecular and dissociative adsorptions were found to be not much favored, in terms of energy, by the surface defects inspected in this study. Although the adsorption on the defective surface takes place at higher energy, it gives longer SO bond enlargement or longer separation between the dissociated atoms, which implies that the defective surface drives enhanced SO activation on the surface. The NBO investigation on the transition state of dissociative adsorption of SO for pre-converged MEP reveals the energy barrier of about 0.6 eV for the clean surface, while it is reduced to 0.12 eV on the Pt doped surface, suggesting the remarkable potential of Pt on single-atom catalysis application. We believe that the guest atom induced reduction in the energy barrier for the dissociation of molecules will promise further single-atom catalysis applications. This report is supposed to aid and/or guide experimentalists giving a good insight on the dissociation of molecules. Besides, the information provided here can be used as a benchmark for further investigation on dissociation of small molecules on the transition metal surfaces, which are highly desirable for catalysis application.

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