

Nonadiabatic Effects in the Molecular Oxidation of Subnanometric Cu₅ Clusters

Published as part of *The Journal of Physical Chemistry virtual special issue "Vincenzo Barone Festschrift"*.

Alexander O. Mitrushchenkov, Alexandre Zanchet, Andreas W. Hauser,*
and María Pilar de Lara-Castells*

Cite This: *J. Phys. Chem. A* 2021, 125, 9143–9150

Read Online

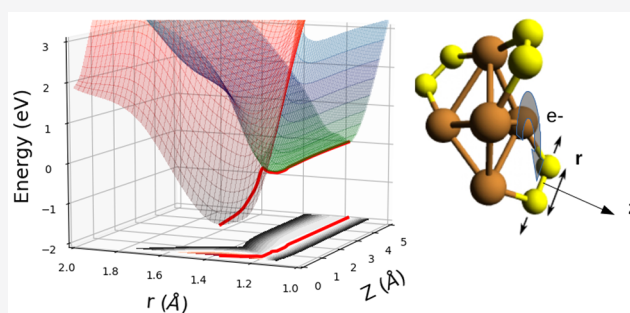
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: The electronic structure of subnanometric clusters, far off the bulk regime, is still dominated by molecular characteristics. The spatial arrangement of the notoriously undercoordinated metal atoms is strongly coupled to the electronic properties of the system, which makes this class of materials particularly interesting for applications including luminescence, sensing, bioimaging, theranostics, energy conversion, catalysis, and photocatalysis. Opposing a common rule of thumb that assumes an increasing chemical reactivity with smaller cluster size, Cu₅ clusters have proven to be exceptionally resistant to irreversible oxidation, i.e., the dissociative chemisorption of molecular oxygen. Besides providing reasons for this behavior in the case of heavy loading with molecular oxygen, we investigate the competition between physisorption and molecular chemisorption from the perspective of nonadiabatic effects. Landau–Zener theory is applied to the Cu₅(O₂)₃ complex to estimate the probability for a switching between the electronic states correlating the neutral O₂ + Cu₅(O₂)₂ and the ionic O₂[−] + (Cu₅(O₂)₂)⁺ fragments in a diabatic representation. Our work demonstrates the involvement of strong nonadiabatic effects in the associated charge transfer process, which might be a common motive in reactions involving subnanometric metal structures.



1. INTRODUCTION

From a chemical point of view the reactivity of molecular oxygen is a complex phenomenon. In the gas phase, the ground state of O₂ is a triplet as the molecule holds two unpaired electrons. However, when reacting with another species M such as a molecule, a metal cluster, or an extended metal-oxide surface, the bonding is generally associated with peroxo (O₂^{2−}) or superoxo (O₂[−]) forms of molecular oxygen.^{1,2} The latter are correlated to excited ionic states of the M–O₂ pair, where the character of the O₂ molecule is either of singlet or doublet spin multiplicity.³ For a better understanding of O₂ reactivity, it is therefore necessary to calculate the transition along the reaction pathway between the triplet O₂ molecule in the gas phase and its associated singlet/doublet peroxo/superoxo form when engaging in chemical bonding.

In biochemistry, a clear preference for spin-saturated closed-shell systems is observed. Reactivity with O₂ is therefore strongly quenched, explaining the stability of organic matter in a rich O₂ environment. Nevertheless, some proteins, e.g., members of the oxygenase family, are capable of catalyzing the reduction of molecular oxygen. Proteins of this kind typically contain a transition metal cofactor that mediates the spin transition. It allows them to activate molecular oxygen and to

initiate reactions such as peroxidation or hydroxylation, which are essential in certain steps of biological synthesis.⁴ Because of their high catalytic activity, oxygenases are widely used in the pharmaceutical industries and play a crucial role in the synthesis of drugs or drugs precursors.⁵ In this work, we have chosen Cu₅ clusters as a nonorganic, industrially accessible equivalent to a biochemistry-inspired transition metal cofactor.

Subnanometric metal clusters have recently emerged as innovative materials for numerous applications in, for example, energy conversion, catalysis^{6–11} and photocatalysis.^{11,12} Moreover, the deposition of small copper and silver clusters onto TiO₂ surfaces has proven useful for the creation of novel visible-light photoactive materials,^{12,13} potential photocatalysts for CO₂ reduction,^{11,14} and two-dimensional (2D) polaronic materials.^{14,15} With regard to bio-oriented applications, the

Received: August 16, 2021

Revised: September 23, 2021

Published: October 11, 2021



chemical and thermodynamical stability of Cu_5 clusters in solution over the whole pH range is particularly promising.¹⁶

Unlike biological systems, which require specific catalytic proteins to reduce molecular oxygen, the Cu_5 cluster is a doublet spin species which can combine with the triplet ground state of O_2 to form spin states of doublet as well as quartet multiplicity, thus facilitating spin transitions. To validate its capability as a reducing agent for O_2 , the interaction between Cu_5 and O_2 needs to be studied in greater detail. Because Cu_5 mediates both singlet and triplet states of O_2 , we can expect that the reactivity between those species involves several electronic configurations and can thus be considered as an, inherently, multireference problem. Their energetic proximity further suggests the presence of significant non-adiabatic effects. This implies that single-reference density functional theory (DFT) or post-Hartree–Fock approaches such as second-order Møller–Plesset (MP2) and coupled-cluster [e.g., CCSD(T)] methods can only deliver an incomplete picture of the reaction mechanism at best,¹⁷ making the application of multireference methods mandatory.

A first evaluation of the Cu_5 catalytic performance employing multireference techniques was performed in ref 18. Despite the well-known tendency to complete oxidation as it is generally observed for Cu nanoparticles, *ex situ* experimental measurements⁶ and theoretical studies considering the adsorption of a single oxygen molecule^{6,18,19} have indicated an unexpected resistivity to the “irreversible” oxidation at temperatures below 423 K for Cu_5 , in both structural motifs identified by theory, i.e., a planar trapezoidal as well as a bipyramidal structure. In the latter case, the O_2 molecule can be easily chemisorbed due to a low barrier to access the well, but the splitting of the O–O bond remained the rate-determining step for an irreversible oxidation to occur.¹⁸ Interestingly, in the case of a single O_2 molecule, the chemisorption well remains relatively shallow, and because the barrier is low, the O_2 molecule may have the possibility to desorb under the right conditions, suggesting the possibility of a “reversible” oxidation.

In this work, the application of multireference *ab initio* theory instead has allowed us to calculate the energy barriers to molecular and dissociative chemisorption when multiple O_2 molecules become adsorbed. In fact, the high symmetry of the bipyramidal isomer of Cu_5 clusters suggests that more than one molecule can be chemisorbed. For instance, previous studies have shown that reduced metal-oxide surfaces are capable of engaging three O_2 molecules per vacancy (in both neutral and reduced molecular forms) at full coverage.² On the other hand, the possible role of nonadiabatic effects on the oxidation of Cu_5 clusters, and more generally of subnanometric metal clusters, in an O_2 -rich environment remains an open question. We consider the particular case of the interaction of a third O_2 molecule with a copper cluster bearing already two O_2 molecules, or, in other words, the $\text{O}_2 + \text{Cu}_5(\text{O}_2)_2$ reaction, and apply multireference *ab initio* theory within a diabatic representation. The consideration of the particular $\text{Cu}_5(\text{O}_2)_3$ system has been motivated by the compensated loading of three O_2 molecules on alternate Cu–Cu bonds.

The article is structured as follows. In section 2 we provide a detailed description of the computational methods. Results are presented in section 3, which includes an extended analysis of the electronic structure of the $\text{Cu}_5(\text{O}_2)_3$ system at the molecular chemisorption state of the diabatic potential energy surfaces correlating with ionic $[\text{O}_2^- + (\text{Cu}_5(\text{O}_2)_2)^+]$ and

neutral $[\text{O}_2 + \text{Cu}_5(\text{O}_2)_2]$ fragments for the $\text{O}_2 + \text{Cu}_5(\text{O}_2)_2$ bimolecular reaction and of the probability of charge transfer within the Landau–Zener model. Our findings are summarized and conclusions are presented in section 4.

2. COMPUTATIONAL METHODS

2.1. Electronic Structure Calculations. Multireference perturbation theory has been applied to determine the reaction pathway of a single O_2 molecule interacting with the $\text{Cu}_5(\text{O}_2)_2$ complex, i.e., a Cu_5 cluster with two O_2 molecules adsorbed. A trigonal-bipyramidal (3D) structure has been assumed for the Cu_5 cluster. The geometry optimization of the $\text{Cu}_5(\text{O}_2)_3$ cluster geometry has been performed at the PBE-D3 level^{20–22} by using the ORCA²³ suite of programs (ver. 4.0.1.2) and the atom-centered def2-TZVP²⁴ basis set for copper and oxygen atoms. The optimized geometry calculated at the DFT-D3 level has been used as an initial guess in follow-up calculations with multireference *ab initio* theory. At the minima, also a single-reference DFT description can offer sufficient accuracy.

We have considered the electronic state correlating with the neutral O_2 and $\text{Cu}_5(\text{O}_2)_2$ fragments in the asymptotic region (termed the neutral state) and that correlating with the ionic O_2^- and $(\text{Cu}_5(\text{O}_2)_2)^+$ ionic systems (termed the ionic state). The combination of doublet (Cu_5) and three triplet (O_2) states results in doublet, quartet, sextet, and octet spin states. The doublet spin state has been considered in our calculations as it is energetically favored at the molecular chemisorption state. However, since the three adsorbed O_2 molecules, with each carrying an unpaired electron, are localized at a larger distance to each other, the energy differences between states with different multiplicity are very small.

As mentioned above, the initial structure for the chemisorption state of the $\text{Cu}_5(\text{O}_2)_3$ complex has been the minimum-energy geometry obtained at the DFT-D3 level. The actual reaction pathway has been approximated by considering the more-involved nuclear degrees of freedom. In particular, in the given scenario, the optimized internuclear O–O distance has been found to differ significantly in neutral and ionic states at the corresponding physisorption and molecular chemisorption energy minima. Therefore, to obtain a sensible estimation of the actual reaction pathway, we have performed a two-dimensional (2D) scan: The first coordinate (Z) is the distance of the oxygen molecule (its center of mass) to the cluster, with $Z = 0$ defined as its optimized position in the chemisorption minimum of the $\text{Cu}_5(\text{O}_2)_3$ complex. The second coordinate is the internuclear O–O distance (r). The remaining degrees of freedom have been kept fixed in these 2D scan calculations. We have applied the single-reference internally contracted RS2C method²⁵ with density fitting (DF-RS2C), as implemented within the MOLPRO program package.²⁶

To calculate the neutral and ionic states, we have followed the methodological strategy proposed in refs 27 and 28 for the interaction of O_2 with a reduced TiO_2 surface. We first optimize the orbitals by using the single-state DF-CASSCF method separately for neutral and ionic states, which allows to calculate directly diabatic states.²⁸ Because neutral and ionic states bear a very different electronic character, the corresponding optimized orbitals for these two states are also very different. Hence, common approaches using a common set of orbitals would require very large configuration interaction (CI) expansions, and the calculation would be computationally unfeasible. The use of orbitals optimized

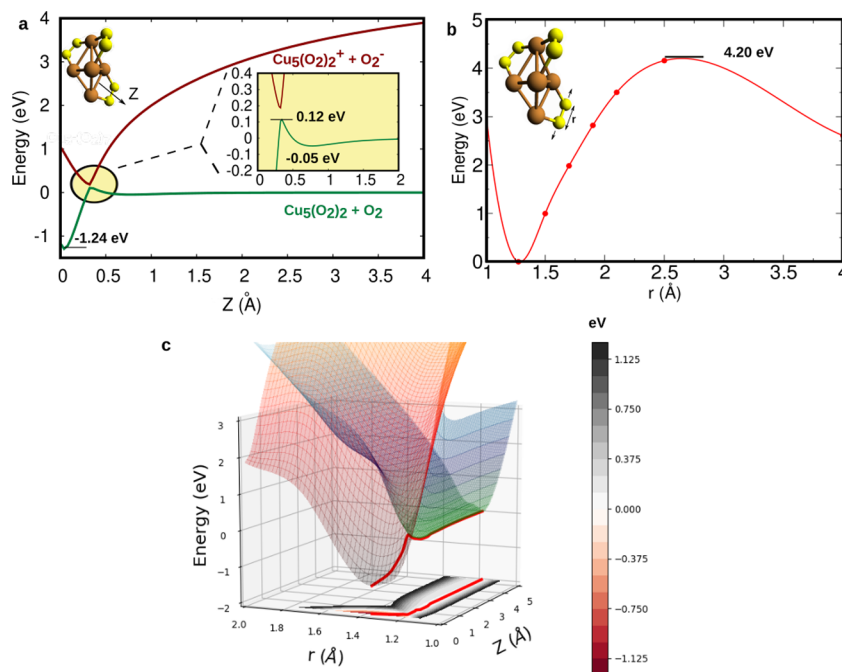


Figure 1. (a) $\text{O}_2 + \text{Cu}_5(\text{O}_2)_2$ reaction energy pathway in the adiabatic representation using the (77) active space. In the reactants region, the neutral state (green) corresponds to the ground state and the ionic pair state (red) corresponds to the excited state. In the chemisorption region, the ground state present ionic character while the neutral state lies higher in energy. For clarity, an expanded view of the region of the barrier is represented showing the avoided crossing between the two states. (b) Potential energy scan providing the energy dependence upon the O–O stretching of one chemisorbed O_2 molecule by using the (13 11) active space. The figure shown in (a) corresponds to a 2D scan in the r and Z coordinates, with the rest of the coordinates having been kept fixed. The Z coordinate in the potential energy curve shown in (b) has been kept fixed instead, with the energies having been given relative to the value obtained at $r = 1.273 \text{ \AA}$. (c) Two-dimensional (2D) representation of the diabatic potential energy surfaces (PES), including the minimum-energy pathway. Contour plot of the ground adiabatic PES and its energy scale are also shown for clarity.

separately for each state is thus natural. To ensure continuous behavior of the electronic structure along Z , we start the calculation at large distance, where the neutral oxygen molecule (and ion) are well separated from the copper cluster. Starting from this distance, we move inward, repeatedly using the electronic wave function of the previous step as a starting guess and ensuring that the orbitals are only modified gradually. At present, this is possible by using the SUPER-CI optimization method²⁹ as implemented in a recent version of the MOLPRO code.³⁰ The DF-CASSCF approach is employed to account for the most important nondynamic correlation effects. Then, the single-reference RS2C method is applied to cover dynamical correlation effects. Because the two diabatic states (ionic and neutral) can cross, it is easy to locate the seam in the 2D representation depending on (r, Z) . The location of the transition state between physisorption and chemisorption states corresponds to the minimum energy crossing point (MECP) between these two diabatic states, being thus given by the position (Z, r) of the minimum of the seam. Similarly to the case of the $\text{O}_2\text{--TiO}_2$ system (see refs 27 and 28), neutral and ionic states are effectively diabatic but nonorthogonal states. The overlap and the transition matrix element of the electronic Hamiltonian between these two states are calculated at the CASSCF level by using the transformation to biorthogonal orbitals as implemented within MOLPRO.³¹ As the two states are nonorthogonal, the unique definition of diabatic states is not possible as it depends on the used orthogonalization method (e.g., symmetric vs Schmidt). Therefore, a transformation to adiabatic states is performed to estimate the effective nonadiabatic interaction. After orthogon-

alization, the transformed 2×2 electronic Hamiltonian is diagonalized to obtain the adiabatic energies that form the avoided crossing. Next, H_{12} can be calculated as the half of the energy difference between the two adiabatic surfaces at the point when this difference is minimal (at the CASSCF level). This value of H_{12} is used together with diabatic energies obtained at the DF-RS2C level.

To carry out the DF-CASSCF/DF-RS2C calculations, we use the polarized correlation-consistent triple- ζ basis of Dunning and collaborators³² (cc-pVTZ) for oxygen atoms and the cc-pVTZ-PP basis set for copper atoms,³³ including a small (10-valence-electron) relativistic pseudopotential. For density fitting, the associated MP2FIT and JKFIT bases were used in CASSCF and RS2C calculations, respectively. For the 2D scans of interactions energies in neutral and ionic states, the active space was built from 7 electrons in 7 orbitals (referred to us as (77) active space), while 68 closed-shell orbitals were fully optimized at the DF-CASSCF level. Of these, 32 core orbitals were not correlated at the DF-RS2C level. To get an estimation of the energy barrier to O_2 dissociation, it was necessary to increase the active space [13 electrons in 11 orbitals, referred to us as (13 11) active space] due to the higher multiconfigurational character of the wave function upon the O–O bond elongation. Additionally, the whole $\text{Cu}_5(\text{O}_2)_3$ structure at the chemisorption minimum was reoptimized at the CASSCF level by using the (13 11) active space, with the optimized r value being 1.273 \AA . Next, the r value was varied, keeping the rest of the coordinates fixed to the corresponding optimized values at the CASSCF-derived

optimized geometry, thus obtaining a potential energy curve as a function of r .

The diagonalization of the first-order reduced density matrix obtained from the wave function in CASSCF calculations allows to obtain natural orbitals. The chemical oxidation states of the copper atoms as well as the reduced forms of the adsorbed O₂ molecules in the Cu₅(O₂)₃ complex have been deduced from an analysis of the Mulliken charges³⁴ and atomic spin populations of the CASSCF-derived natural orbitals with the Hirshfeld method.^{35,36}

2.2. Landau–Zener Model. To estimate the electron hopping probability between the diabatic electronic states of the O₂–Cu₅(O₂)₂ complex correlating with neutral and ionic fragments, we apply the Landau–Zener (LZ) model.^{37–39} Within the LZ model, the electron hopping probability can be defined as $1 - P_{LZ}$, with P_{LZ} being the LZ probability for a nonadiabatic transition:

$$P_{LZ}(v) \approx \exp[(-2\pi H_{12}^2)/(F_{12}v)] \quad (1)$$

In eq 1, v is the relative velocity of the fragments, F_{12} is the difference between the two slopes F_1 and F_2 of the diabatic potential energy surfaces at the intersection between the neutral and ionic states, and H_{12} is the off-diagonal matrix element of the electronic Hamiltonian. Assuming a Maxwell–Boltzmann (MB) distribution for the relative velocities of the reactants, the electron hopping probability can be written as a function of temperature. For this purpose, we integrated over the hopping probabilities from the LZ model, P_{LZ} , expressed as a function of the velocity v in the reaction coordinate (i.e., defining the minimum-energy pathway), and weighted with a Boltzmann factor P_{MB}

$$P_{LZ}(T) \approx \int dv P_{LZ}(v)P_{MB}(v) \quad (2)$$

where $P_{MB}(v)$ denotes the MB distribution of relative velocities in one direction

$$P_{MB}(v) = \left(\frac{\mu}{2\pi k_B T} \right)^{1/2} e^{-\mu v^2/2k_B T} \quad (3)$$

with k_B as the Boltzmann constant.

3. RESULTS AND DISCUSSION

3.1. Chemisorption Minima. Oxidation States of Cu Atoms. Reactivity with molecular oxygen is generally associated with strong electronic correlation effects, making the assignment of oxidation–reduction states complicated in high level *ab initio* calculations. In this sense, one key advantage of the diabatic representation is that the character of the wave function is preserved along the reaction path (see, e.g., ref 28). This feature can be used as an useful interpretative tool to identify the oxidation–reduction states, particularly in the case of O₂. Indeed, in the asymptotic region, the two fragments [i.e., O₂ and Cu₅(O₂)₂] are not interacting. Hence, the simple inspection of the orbital occupation numbers allows to determine the states corresponding to neutral and ionic interacting pairs. By following these states diabatically along the reaction path, it is possible to assign the correct reduction state. The region of electron transfer corresponds to the crossing between ionic and neutral states.^{3,28}

It can be observed in Figure 1 that the chemisorption well of the Cu₅(O₂)₃ complex correlates directly with the ionic O₂[−] + (Cu₅(O₂)₂)⁺ interacting pair. This implies that the incoming

oxygen molecule captures an electron from the Cu₅(O₂)₂ complex, becoming chemisorbed as a superoxo ion O₂[−]. A Mulliken charge analysis of the natural orbitals can be applied to determine the reduction state of the remaining two O₂ molecules. The analysis of the more stable structure shown in Figure 2 reveals that the three O₂ molecules of the Cu₅(O₂)₃

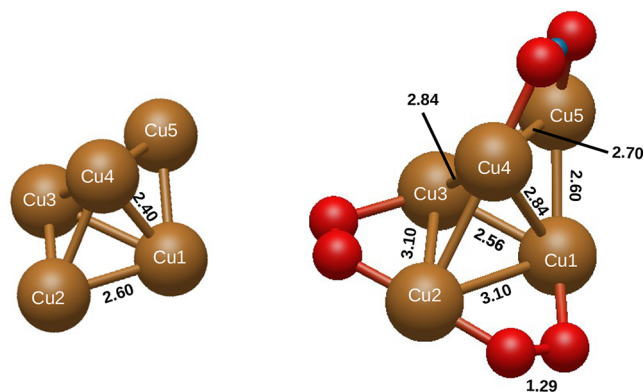


Figure 2. Geometry of the bare Cu₅ cluster (left panel) and the Cu₅(O₂)₃ complex (right panel). Values of internuclear distances are given in angstroms. Symmetry-equivalent Cu–Cu distances have been skipped in the figure (e.g., the value of the Cu1–Cu3 distance in the panel on the left is 2.40 Å due to the symmetry of the trigonal bipyramidal Cu₅ structure).

complex at the chemisorption minimum bear a similar charge of ca. −0.7 lel. It is known that the Mulliken analysis tends to underestimate the degree of ionicity but remains globally proportional to the real charge distribution. Because the incoming O₂ molecule becomes absorbed as a superoxo O₂[−] radical, it follows that all the three O₂ molecules are attached to the copper cluster as O₂[−] species, with each of them having taken one electron from the Cu₅ cluster.

The assignment of reduction states is further confirmed by the analysis of spin atomic populations, which indicates the existence of three unpaired electrons when three O₂ molecules become chemisorbed onto the copper cluster. From the analysis of the multireference wave function, it is also clear that all O₂ molecules in the Cu₅(O₂)₃ complex can be characterized by a spin of almost unity, confirming the superoxo O₂[−] radical nature of the three chemisorbed O₂ molecules.

The conversion of the three O₂ molecules in superoxo species is also reflected in the enlargement of the O–O bond lengths (larger than ca. 1.3 Å) upon from the value for the neutral O₂ molecule (ca. 1.2 Å). The inclusion of the dispersion interaction via the D3 *ansatz*²¹ in the DFT-based description is in fact correlated to the enlargement of the Cu–Cu bonds, as necessary to accommodate the superoxo species with larger O–O bond lengths than for the neutral O₂ molecule. The reoptimization of the structure using the D4 Grimme’s parametrization⁴⁰ modifies the Cu–Cu bond length by less than 10^{−3} Å.

Having confirmed the reduction state of the chemisorbed oxygen molecules, it is also possible to extract the individual oxidation numbers for the copper atoms from the Mulliken charge analysis. The copper atoms labeled as Cu1, Cu3, Cu4, and Cu5 in Figure 2 bear a positive charge of 0.35 lel each. In contrast, the copper atom labeled Cu2, located between the two O₂ molecules, has a positive charge of 0.7 lel, which is identical in size to the negative charges assigned to the O₂

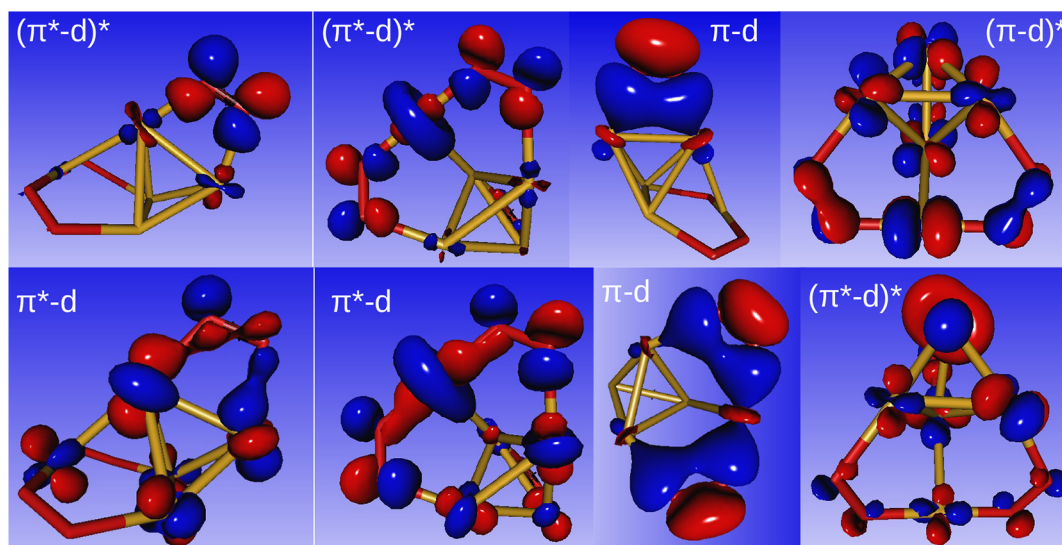


Figure 3. Main (natural) orbitals involved in the bonding between the Cu_5 cluster and the three adsorbed O_2 molecules in the $\text{Cu}_5(\text{O}_2)_3$ complex. Note the pronounced bonding between $3d(\text{Cu})$ and $\pi(\text{O}_2)$ orbitals.

molecules. It can therefore be concluded that the Cu2 atom exhibits a net positive charge, while the remaining positive charges are delocalized over the other four copper atoms. We note that the Cu2 atom differs from the others in being the only atom bonded to two O_2 molecules. On average, half an electron is provided from each Cu atom to the bonded oxygen atom. Such partial values of the charges are indicative of a concerted, collaborative behavior between all Cu atoms for charge transfer, which is attributed to a complex metal–ligand bonding scheme involving the d orbital network of the Cu_5 cluster with both the π and π^* orbitals of the adsorbed O_2 molecules, as can be readily seen in Figure 3.

The modification of the Cu_5 electronic structure and geometry upon adsorption of three molecules compared with that of the bare Cu_5 cluster invokes the concept of structural fluxionality of metal clusters at the subnanometric scale, a feature with the potential to enhance its catalytic activity¹¹ (see also, e.g., ref 41). Of course, many local minima associated with different positions of the three adsorbed O_2 molecules might have similar energies to that calculated for the global minimum at the chemisorption state. Such energy landscape is implicitly associated with fluxional dynamics and wide amplitude motions in the $\text{Cu}_5(\text{O}_2)_3$ complex where the O_2 molecules can readily exchange positions. An important role of structural fluxionality has been recently advocated for Ni_5 clusters having a trigonal-bipyramidal 3D structure with an intruder Au atom, enhancing the weight of the configurational entropy.⁴² The occurrence of a fluxional dynamics on cationic Cu_5^+ clusters has been also suggested from recent IR spectroscopic characterizations of H_2 adsorption.⁴³

3.2. Potential Energy Surfaces in a Diabatic Representation. As mentioned in the Computational Methods section, the neutral and ionic states characterizing the $\text{O}_2\text{--Cu}_5(\text{O}_2)_2$ interaction are calculated in a similar way to that employed in a previous study of the “molecular” oxidation of a reduced $\text{TiO}_2(110)$ surface (see ref 28). The ionic state, which is the ground state at the chemisorption minimum, is characterized by a strong Coulombic interaction between a negatively charged superoxo O_2^- radical and a positively charged $(\text{Cu}_5\text{--}(\text{O}_2)_2)^+$ system. It is asymptotically correlated to a separation in charged fragments O_2^- and $(\text{Cu}_5(\text{O}_2)_2)^+$. In

contrast, the neutral state corresponds to the interaction between neutral fragments and leads to a separation into an oxygen molecule and the $\text{Cu}_5(\text{O}_2)_2$ complex. This state is the ground state at the physisorption minimum, as shown in Figure 1a. The wave function at the transition state (TS) geometry between chemisorption and physisorption shows a strong multiconfigurational character. The same holds for the TS geometry at O_2 dissociation, which reconfirms the necessity of a multireference method for an appropriate analysis of the reaction pathway. A barrier height of 0.12 eV is obtained, which is comparable to that published in ref 18 (0.09 eV), where only one O_2 molecule was considered for the first step of the oxidation of Cu_5 . It is interesting to observe that chemisorbed O_2 molecules are barely affecting the height of the barriers in successive molecular oxidation steps.

In contrast, an interesting collaborative effect involving delocalized d-type orbitals of the Cu atoms is found with regards to the stability of the chemisorption well, which is much deeper (−1.16 eV) in the case of the $\text{O}_2 + \text{Cu}_5(\text{O}_2)_2$ reaction than in the first oxidation step of the Cu_5 cluster. As can be observed in Figure 1a, despite this collaborative effect, due to the high energy of the excited state correlating with the $\text{O}_2^- + (\text{Cu}_5(\text{O}_2)_2)^+$ fragments, the oxygen molecule is released as a neutral molecule. In other words, a net charge on the cluster oxide $\text{Cu}_5(\text{O}_2)_2$ as an independent species is energetically forbidden: it loses an electron when the O_2 molecule is adsorbed but recovers it upon O_2 desorption. This is a direct consequence of the high ionization potential exhibited by the subnanometric copper cluster.

To ensure that the oxidation is indeed reversible, in addition to discarding the possibility of chemical ionization, it is further necessary to check whether the O_2 molecules can dissociate or not. In fact, because the collaborative effect induces a larger stability than a single O_2 molecule, one may wonder if this extra energy allows the O_2 molecule to dissociate on the cluster. Figure 1b indicates that it is not the case. The estimated value of the energy required to dissociate O_2 is higher than 4 eV, much larger than the extra stability provided by the collaborative effect and very similar to the case of single O_2 adsorption.¹⁸ The reason for the estimated high value of the energy barrier to O_2 dissociation is attributed to the complex

binding network formed between the O₂ molecules and the Cu₅ clusters. By relaxing the whole Cu₅(O₂)₃ complex at the *r* value associated with the TS state (2.5 Å), the energy barrier becomes lower by only 0.2 eV at the CASSCF level. Therefore, it is improbable that even considering higher levels of *ab initio* theory, it gets flat enough to render the breaking of the O₂ bond kinetically allowed at room and experimentally relevant temperatures.

An illustration of the collaborative effect mentioned above is given in Figure 3. The very favorable overlap between the π and π^* orbitals of O₂ with d-type orbitals of Cu₅ gives rise to a complex and stable π -d- π^* molecular orbital network. Interestingly, not only the frontier orbitals are involved, but also π -type and inner d-type orbitals are contributing to the chemical engagement between copper and oxygen atoms. To break the O–O bond, in addition to the intrinsic dissociation energy of molecular oxygen, it would be necessary to provide additional energy input to fragment this complex π -d- π^* orbital network. The involvement of π^* orbitals is a classic case of back-bonding and an intermediate state of O–O bond dissociation. However, the fact that the usual electron transfer from bonding into antibonding orbitals is coupled to the sterically less flexible Cu₅ orbital network makes the O–O bond rupture energetically more costly.

3.3. Landau–Zener Model. Within the Landau–Zener model, the probability for electron hopping from the Cu₅(O₂)₂ complex to an incoming O₂ molecule is predicted to decrease—and thus the Cu(I) proportion—as the temperature increases (see Figure 4). This outcome can be interpreted as

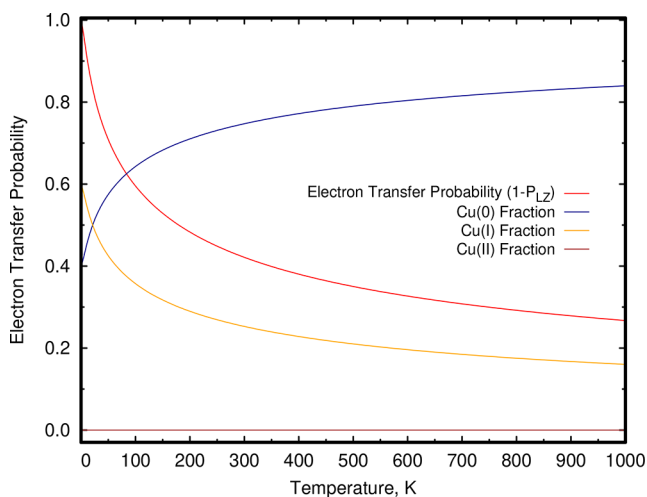


Figure 4. Electron hopping probability as a function of the kinetic temperature in the reaction coordinate. Probability of electron hopping ($1 - P_{LZ}$) from the copper cluster of the Cu₅(O₂)₂ complex to an incoming O₂ molecule within the Landau–Zener model for nonadiabatic transitions.³⁹ The fraction of the oxidation copper state Cu(I) is also shown. It has been estimated as $(1 - P_{LZ}) \times f_{Cu(I)}$, with $f_{Cu(I)}$ the fraction of the Cu(I) state in the Cu₅(O₂)₃ complex (calculated at the same level of theory as the diabatic electronic states).

follows: On one hand, similarly to a charge transfer harpoon-type reaction,³⁹ lower temperatures imply lower relative velocities of the reactant species (i.e., the incoming O₂ molecule and the Cu₅(O₂)₂ complex). On the other hand, lower velocities favor the electron hopping process because more time is spent at the crossing region between the diabatic

electronic states correlating with ionic and neutral fragments. Because of the smaller value of the H_{12} as compared to the case of the Cu₅–O₂ complex (see ref 18), the probability for the Cu₅(O₂)₃ complex to remain neutral as the temperature increases becomes much larger. As discussed in ref 18, the LZ probability of nonadiabatic transitions for the O₂ + Cu₅ system is very small so that the height of adiabatic energy barrier from physisorbed to molecular chemisorbed states determines accessibility of the latter at a given temperature. For the Cu₅ cluster having a 3D structure, such a barrier is very small (0.09 eV, see ref 18) so that the chemisorption state is accessible even at room temperature. In stark contrast, the barrier for the Cu₅ cluster having a planar structure is very large, avoiding accessibility at room and higher temperatures.¹⁸ Hence, our results indicate the enhancement of nonadiabatic effects upon adsorption of multiple O₂ molecules on the Cu₅ cluster. Although the LZ model has just been applied to a particular collision event, it might be representative of the physics occurring at ultrahigh vacuum (UHV) when molecular beams of O₂ are scattered by Cu₅ clusters (i.e., when the kinetic regime of bimolecular collisions is dominating).

Summarizing this section, by including nonadiabatic effects via the LZ model, the probability of electron hopping from the Cu₅(O₂)₂ complex to an incoming O₂ molecule is predicted to decrease—and then the proportion of the oxidated Cu(I) form—as the (LZ) temperature increases since, as mentioned above, higher velocities reduce the time spent in the crossing region between the diabatic states correlating with ionic and neutral fragments.

4. CONCLUSIONS

The application of multireference perturbation theory to the O₂–Cu₅ system¹⁸ and the O₂–Cu₅(O₂)₂ complex indicates high energy barriers for O₂ dissociation. Conversely, the energetic barriers to reach the molecular chemisorption states from the physisorption counterparts are very low (ca. 0.1 eV, see Figure 1a). Hence, the oxidation is expected to be reversible even if several O₂ molecules are chemisorbed. From a broader perspective, our findings underline the key role of nonadiabatic effects in the charge transfer process characterizing the O₂ + Cu₅(O₂)₂ bimolecular collision. The electronic structure of the complex is strongly affected by the somewhat “floppy” character of the cluster geometry, which gives rise to pronounced nonadiabatic effects. Similar tendencies are expected to be rather general for charge transfer processes between molecular systems and subnanometric metal clusters. Temperature-dependent experimental studies, using molecular beams of O₂ scattered by subnanometric metal clusters at ultrahigh vacuum, would provide very useful insights into the described reduction process upon heating and its underlying nonadiabatic effects. Nonadiabatic multidimensional quantum dynamics calculations on the molecular oxidation of subnanometric clusters would be also very valuable in delivering mechanistic information about the interplay between fluxional dynamics and charge transfer.

In conclusion, our results indicate that Cu₅ clusters are industrially feasible candidates for the mediation of chemical reactions involving spin transitions such as the reduction of molecular oxygen. An extension toward biochemical applications will necessitate a further theoretical assessment of Cu₅ in solution and in biological environments, preferably starting with a modeling of the same process in water. To render the calculation computationally feasible, the application of polar-

izable continuum models such as those developed by Barone and co-workers seem promising.^{44–48} Early work on nucleobases, combining hybrid HF/DFT PBE0 and time-dependent PBE0 treatments with a multiconfigurational *ab initio* description to locate conical intersections, appears particularly reassuring.⁴⁹

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c07271>.

Cluster geometries in Cartesian coordinates of the most relevant structures of the $\text{Cu}_5(\text{O}_2)_3$ complex at the (1) the minimum-energy crossing point between ionic and neutral states, (2) the molecular chemisorption minimum, and (3) the transition state between molecular and dissociative chemisorption states (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Andreas W. Hauser – Institute of Experimental Physics, Graz University of Technology, 8010 Graz, Austria; orcid.org/0000-0001-6918-3106; Email: andreas.w.hauser@gmail.com

María Pilar de Lara-Castells – Instituto de Física Fundamental (AbinitSim Unit), CSIC, 28006 Madrid, Spain; orcid.org/0000-0001-8697-5770; Email: Pilar.deLara.Castells@csic.es

Authors

Alexander O. Mitrushchenkov – MSME, UPEC, CNRS, Université Gustave Eiffel, F-77454 Marne-la-Vallée, France

Alexandre Zanchet – Instituto de Física Fundamental (AbinitSim Unit), CSIC, 28006 Madrid, Spain

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpca.1c07271>

Notes

The authors declare no competing financial interest. The data supporting the results presented in this work are available from the corresponding authors on reasonable request.

■ ACKNOWLEDGMENTS

We thank M. Arturo López-Quintela and Félix G. Requejo for sharing their most recent experimental insights into the reversible oxidation of Cu_5 clusters in numerous discussions. This work has been partly supported by the Spanish Agencia Estatal de Investigación (AEI) and the Fondo Europeo de Desarrollo Regional (FEDER, UE) under Grants PID2020-117605GB-I00, MAT2016-75354-P, and PID2019-107115GB-C21 as well as the Austrian Science Fund (FWF) under Grant P29893-N36. The CESGA supercomputer center (Spain) and the CTI-CSIC are acknowledged for having provided computational resources.

■ REFERENCES

(1) de Lara-Castells, M. P.; Krause, J. L. Periodic Hartree–Fock Study of the Adsorption of Molecular Oxygen on a Reduced $\text{TiO}_2(110)$ Surface. *J. Chem. Phys.* **2001**, *115*, 4798–4810.

(2) de Lara-Castells, M. P.; Krause, J. L. Theoretical Study of the Interaction of Molecular Oxygen with a Reduced TiO_2 Surface. *Chem. Phys. Lett.* **2002**, *354*, 483–490.

(3) Ortega, P.; Gil-Guerrero, S.; Veselinova, A.; Zanchet, A.; Gonzalez-Sanchez, L.; Jambrina, P. G.; Sanz-Sanz, C. DpgC-Catalyzed Peroxidation of 3,5-Dihydroxyphenylacetyl-CoA (DPA-CoA): Insights into the Spin-Forbidden Transition and Charge Transfer Mechanisms. *J. Chem. Phys.* **2021**, *154*, 144303.

(4) Elwell, C. E.; Gagnon, N. L.; Neisen, B. D.; Dhar, D.; Spaeth, A. D.; Yee, G. M.; Tolman, W. B. Copper-Oxygen Complexes Revisited: Structures, Spectroscopy, and Reactivity. *Chem. Rev.* **2017**, *117*, 2059–2107.

(5) Chaturvedi, S. S.; Ramanan, R.; Lehnert, N.; Schofield, C. J.; Karabencheva-Christova, T. G.; Christov, C. Z. Catalysis by the Non-Heme Iron(II) Histone Demethylase PHF8 Involves Iron Center Rearrangement and Conformational Modulation of Substrate Orientation. *ACS Catal.* **2020**, *10*, 1195–1209.

(6) Concepción, P.; Boronat, M.; García-García, S.; Fernández, E.; Corma, A. Enhanced Stability of Cu Clusters of Low Atomicity Against Oxidation. Effect on the Catalytic Redox Process. *ACS Catal.* **2017**, *7*, 3560–3568.

(7) Halder, A.; Curtiss, L. A.; Fortunelli, A.; Vajda, S. Perspective: Size Selected Clusters for Catalysis and Electrochemistry. *J. Chem. Phys.* **2018**, *148*, 110901.

(8) Hirabayashi, S.; Ichihashi, M. Catalytic Oxidation of CO with N_2O on Isolated Copper Cluster Anions. *Phys. Chem. Chem. Phys.* **2014**, *16*, 26500–26505.

(9) Yang, B.; Liu, C.; Halder, A.; Tyo, E. C.; Martinson, A. B. F.; Seifert, S.; Zapol, P.; Curtiss, L. A.; Vajda, S. Copper Cluster Size Effect in Methanol Synthesis from CO_2 . *J. Phys. Chem. C* **2017**, *121*, 10406–10412.

(10) Maity, P.; Yamazoe, S.; Tsukuda, T. Dendrimer-Encapsulated Copper Cluster as a Chemoselective and Regenerable Hydrogenation Catalyst. *ACS Catal.* **2013**, *3*, 182–185.

(11) López-Caballero, P.; Hauser, A. W.; de Lara-Castells, M. P. Exploring the Catalytic Properties of Unsupported and TiO_2 -Supported Cu_5 Clusters: CO_2 Decomposition to CO and CO_2 Photoactivation. *J. Phys. Chem. C* **2019**, *123*, 23064–23074.

(12) de Lara-Castells, M. P.; Hauser, A. W.; Ramallo-López, J. M.; Buceta, D.; Giovanetti, L. J.; López-Quintela, M. A.; Requejo, F. G. Increasing the Optical Response of TiO_2 and Extending it into the Visible Region through Surface Activation with Highly Stable Cu_5 Clusters. *J. Mater. Chem. A* **2019**, *7*, 7489–7500.

(13) de Lara-Castells, M. P.; Cabrillo, C.; Micha, D. A.; Mitrushchenkov, A. O.; Vazhappilly, T. Ab Initio Design of Light Absorption Through Silver Atomic Cluster Decoration of TiO_2 . *Phys. Chem. Chem. Phys.* **2018**, *20*, 19110–19119.

(14) López-Caballero, P.; Ramallo-López, J. M.; Giovanetti, L. J.; Buceta, D.; Miret-Artés, S.; López-Quintela, M. A.; Requejo, F. G.; de Lara-Castells, M. P. Exploring the Properties of Ag_5 - TiO_2 Interfaces: Stable Surface Polaron Formation, UV-Vis Optical Response, and CO_2 Photoactivation. *J. Mater. Chem. A* **2020**, *8*, 6842–6853.

(15) López-Caballero, P.; Miret-Artés, S.; Mitrushchenkov, A. O.; de Lara-Castells, M. P. Ag_5 -Induced Stabilization of Multiple Surface Polarons on Perfect and Reduced TiO_2 Rutile (110). *J. Chem. Phys.* **2020**, *153*, 164702.

(16) Huseyinova, S.; Blanco, J.; Requejo, F. G.; Ramallo-López, J. M.; Blanco, M. C.; Buceta, D.; López-Quintela, M. A. Synthesis of Highly Stable Surfactant-free Cu_5 Clusters in Water. *J. Phys. Chem. C* **2016**, *120*, 15902–15908.

(17) Ortega, P.; Gil-Guerrero, S.; Veselinova, A.; Zanchet, A.; Gonzalez-Sanchez, L.; Jambrina, P.; Sanz-Sanz, C. Multi- and Single-Reference Methods for the Analysis of Multi-State Peroxidation of Enolates. *Chem. - Eur. J.* **2021**, *27*, 1700–1712.

(18) Zanchet, A.; López-Caballero, P.; Mitrushchenkov, A. O.; Buceta, D.; López-Quintela, M. A.; Hauser, A. W.; de Lara-Castells, M. P. On the Stability of Cu_5 Catalysts in Air Using Multireference Perturbation Theory. *J. Phys. Chem. C* **2019**, *123*, 27064–27072.

- (19) Fernández, E.; Boronat, M.; Corma, A. Trends in the Reactivity of Molecular O₂ with Copper Clusters: Influence of Size and Shape. *J. Phys. Chem. C* **2015**, *119*, 19832–19846.
- (20) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (21) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (22) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (23) Neese, F. Software Update: the ORCA Program System, Version 4.0. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2018**, *8*, e1327.
- (24) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- (25) Celani, P.; Werner, H.-J. Multireference Perturbation Theory for Large Restricted and Selected Active Space Reference Wave functions. *J. Chem. Phys.* **2000**, *112*, 5546–5557.
- (26) Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Lindh, R.; Mitrushchenkov, A. O.; Rauhut, G.; et al. MOLPRO, the most recent version, a package of ab initio programs; see <http://www.molpro.net>, 2018.
- (27) de Lara-Castells, M. P.; Krause, J. L. Theoretical Study of the UV-induced Desorption of Molecular Oxygen from the Reduced TiO₂(110) Surface. *J. Chem. Phys.* **2003**, *118*, 5098–5105.
- (28) de Lara-Castells, M. P.; Mitrushchenkov, A. O.; Roncero, O.; Krause, J. L. Adsorption and Nonadiabatic Processes in the Photodesorption of Molecular Oxygen from the Reduced TiO₂(110) Surface. *Isr. J. Chem.* **2005**, *45*, 59–76.
- (29) Kreplin, D. A.; Knowles, P. J.; Werner, H.-J. Second-Order MCSCF Optimization Revisited. I. Improved Algorithms for Fast and Robust Second-Order CASSCF Convergence. *J. Chem. Phys.* **2019**, *150*, 194106.
- (30) Werner, H.-J.; Knowles, P. J.; Manby, F. R.; Black, J. A.; Doll, K.; Heßelmann, A.; Kats, D.; Köhn, A.; Korona, T.; Kreplin, D. A.; et al. The Molpro Quantum Chemistry Package. *J. Chem. Phys.* **2020**, *152*, 144107.
- (31) Mitrushchenkov, A.; Werner, H.-J. Calculation of Transition Moments between Internally Contracted MRCI Wave Functions with Non-Orthogonal Orbitals†. *Mol. Phys.* **2007**, *105*, 1239–1249.
- (32) Woon, D. E.; Dunning, T. H., Jr. Gaussian Basis Sets for Use in Correlated Molecular Calculations. Calculation of Static Electrical Response Properties. *J. Chem. Phys.* **1994**, *100*, 2975–2988.
- (33) Figgen, D.; Rauhut, G.; Dolg, M.; Stoll, H. Energy-Consistent Pseudopotentials for Group 11 and 12 Atoms: Adjustment to Multi-configuration Dirac–Hartree–Fock Data. *Chem. Phys.* **2005**, *311*, 227–244.
- (34) Mulliken, R. S. Criteria for the Construction of Good Self-Consistent-Field Molecular Orbital Wave Functions, and the Significance of LCAO-MO Population Analysis. *J. Chem. Phys.* **1962**, *36*, 3428–3439.
- (35) Hirshfeld, F. L. Bonded-Atom Fragments for Describing Molecular Charge Densities. *Theor. Chim. Acta* **1977**, *44*, 129–138.
- (36) Bultinck, P.; Van Alsenoy, C.; Ayers, P. W.; Carbó-Dorca, R. Critical Analysis and Extension of the Hirshfeld Atoms in Molecules. *J. Chem. Phys.* **2007**, *126*, 144111.
- (37) Landau, L. D. Zur Theorie der Energieübertragung. II. *Phys. Z. Sowjetunion* **1932**, *2*, 46–51.
- (38) Zener, C. Non-Adiabatic Crossing of Energy Levels. *Proc. R. Soc. London, Ser. A* **1932**, *137*, 696–702.
- (39) de Lara-Castells, M. P.; Hauser, A. W.; Mitrushchenkov, A. O. Ab Initio Confirmation of a Harpoon-Type Electron Transfer in a Helium Droplet. *J. Phys. Chem. Lett.* **2017**, *8*, 4284–4288.
- (40) Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A Generally Applicable Atomic-Charge Dependent London Dispersion Correction. *J. Chem. Phys.* **2019**, *150*, 154122.
- (41) Zhang, Z.; Zandkarimi, B.; Alexandrova, A. N. Ensembles of Metastable States Govern Heterogeneous Catalysis on Dynamic Interfaces. *Acc. Chem. Res.* **2020**, *53*, 447–458.
- (42) López-Caballero, P.; Garsed, R.; de Lara-Castells, M. P. Computational Characterization of the Intermixing of Iron Triade (Fe, Co, and Ni) Surfaces and Sub-nanometric Clusters with Atomic Gold. *ACS Omega* **2021**, *6*, 16165–16175.
- (43) Lushchikova, O. V.; Tahmasbi, H.; Reijmer, S.; Platte, R.; Meyer, J.; Bakker, J. M. IR Spectroscopic Characterization of H₂ Adsorption on Cationic Cus_n⁺ (n = 4–7) Clusters. *J. Phys. Chem. A* **2021**, *125*, 2836–2848.
- (44) Cossi, M.; Barone, V. Analytical Second Derivatives of the Free Energy in Solution by Polarizable Continuum Models. *J. Chem. Phys.* **1998**, *109*, 6246–6254.
- (45) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Polarizable Dielectric Model of Solvation with Inclusion of Charge Penetration Effects. *J. Chem. Phys.* **2001**, *114*, 5691–5701.
- (46) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. New Developments in the Polarizable Continuum Model for Quantum Mechanical and Classical Calculations on Molecules in Solution. *J. Chem. Phys.* **2002**, *117*, 43–54.
- (47) Barone, V.; Cossi, M.; Tomasi, J. Geometry Optimization of Molecular Structures in Solution by the Polarizable Continuum Model. *J. Comput. Chem.* **1998**, *19*, 404–417.
- (48) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, Structures, and Electronic Properties of Molecules in Solution with the C-PCM Solvation Model. *J. Comput. Chem.* **2003**, *24*, 669–681.
- (49) Santoro, F.; Barone, V.; Gustavsson, T.; Improta, R. Solvent Effect on the Singlet Excited-State Lifetimes of Nucleic Acid Bases: A Computational Study of 5-Fluorouracil and Uracil in Acetonitrile and Water. *J. Am. Chem. Soc.* **2006**, *128*, 16312–16322.