

Quantum Monte Carlo Approach for Determining the Activation Barrier of Water Addition to Carbon Monoxide Adsorbed on Pt(111) within 1 kJ/mol

Rajesh O. Sharma, Tapio T. Rantala, and Philip E. Hoggan*



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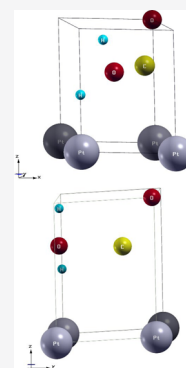


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ABSTRACT: Quantum Monte Carlo (QMC) methods offer *ab initio* calculations of remarkable accuracy for reaction activation barriers (to 1 kJ/mol or 0.01 eV), even at solid surfaces. Chemical reactions generally involve bond dissociation that is poorly described by Hartree–Fock and density functional theory (DFT) methods. However, such processes are often the key to rate-limiting reaction steps at solid surfaces. In this work, a novel QMC methodology is demonstrated as a solution. Carbon monoxide (CO) on platinum reacts with water, first giving the addition products. QMC methods are used here to investigate addition at close-packed Pt(111). The CO is preadsorbed on Pt(111). First, an approaching water molecule is only partially dissociated. At the same time, its oxygen atom binds to CO giving an adsorbed formate moiety (COOH) and Pt–H. This concerted addition is rate-limiting. The QMC activation barrier (in kJ/mol) is 71.0 ± 0.7 , and its apparent measured value is 71.4. This showcases QMC as a method to investigate related catalytic systems.



INTRODUCTION

Quantum Monte Carlo (QMC) methods allow small energy differences to be resolved (*i.e.*, determined) very accurately. An effective strategy helps us to compare the same atoms in two geometries. Precise access to energy and other physical observables of importance to chemistry results. QMC methods for periodic systems (like metals) and their surfaces are being developed, even when they interact with reacting molecules. Reactions involve bond breaking and formation, only accessible to Hartree–Fock approaches when followed by a large configuration interaction (CI) in a multireference (MR) context. This multireference procedure is required to describe dissociation with observed products. The CI could ideally be full CI (FCI). At present, the FCI procedure is limited to modest active space sizes (around 20–40 electrons depending on computational resources). Size restrictions are partly circumvented with a small molecular active site that describes the reaction and is embedded into a periodic wave function. The number of active electrons (and bonds) for FCI or MRCI calculation is limited by including few solid (*e.g.*, metal) atoms. This MRCI is then re-expanded in a suitable basis, to smoothly combine it with the solid periodic basis. Such trial wave functions initialize our QMC work.

The QMC approach used here thus includes an active site, aiming to eventually provide an accurate and feasible *ab initio* approach to heterogeneous catalysis. The first step in the water–gas shift reaction on platinum is water addition to preadsorbed carbon monoxide. This takes place at the Pt(111) face¹ ultimately producing H₂ as a clean, sustainable fuel. In the present work, we evaluate the activation barrier for this

water addition, to showcase the accuracy of QMC. Platinum is represented by a five-layer slab, with planar Pt(111) faces. The active site structure has one surface Pt-atom coordinating a water H-atom at the origin and another Pt-atom defining the apex of an equilateral triangle.

CO adsorbed by its carbon atom in a hollow site above these three Pt atoms is the initial reference. Topologically, the “transition-state” (TS) molecular site is Pt–H and H–O–(Pt)–C=O.

This so-called TS (local and activated) structure occurs between Pt–H–O–H (from adsorbed water) with vicinal Pt–CO (preadsorbed CO) and Pt–H with vicinal Pt–CO–OH (formate) as addition products formed afterward. The formate is a reaction intermediate that is relatively stable. The TS corresponds to the maximum energy on the reaction path between the initial reference and the first intermediate structure (*i.e.*, formate: Pt–CO–OH). Obviously, all-electron calculations at the FCI level are inaccessible for this system; therefore, we use an effective core potential (ECP) to generate the MRCI wave function and the corresponding pseudo-potential (PP) for QMC. That chosen has $Z = 60$ for Pt (instead of the full $Z = 78$) leaving 18 valence electrons per

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67 platinum atom. Including two Pt-atoms in the active site brings
68 it close to the current active-space size limit for FCI, and the
69 trial wave function has selected MRCI determinants with
70 weights above a threshold which restricts the number of
71 determinants retained to one in four. Nevertheless, QMC
72 recovers well from trial wave functions of moderate accuracy,
73 provided that its nodal structure resembles that of the exact
74 wave function.

75 An approximation in our model stems from evidence of
76 rough and nonplanar “111” faces in real systems after
77 relaxation to reduce surface formation energy.² Even so, the
78 present QMC and measured apparent activation energy values
79 differ by less than our statistical error.

80 Nowadays, stochastic methods are increasingly useful
81 innovative electronic structure approaches to work on those
82 challenging systems which require electron correlation
83 accurately. Molecule-solid interactions, for heterogeneous
84 catalysis, are a growth area of these applications, for example,
85 for adsorbed reactions on metals. The water–gas shift reaction
86 (wgs) which follows the overall equation: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2$
87 + H_2 is an industrially important example.³

88 On a Pt(111) surface, step-by-step water dissociation
89 followed by OH and a radical attack of CO were rejected in
90 favor of a concerted, partial water dissociation, while the water
91 oxygen already began to bind to the CO carbon, on the basis of
92 our previous evaluation of the water dissociation barrier which
93 was significantly higher.⁴

94 A full study of this mechanism on Pt, including experiment,
95 density functional theory (DFT), and kinetics, is proposed in
96 the review.⁵ The electron correlation energy contribution
97 varies dramatically during adsorption and reaction; hence, it
98 must be determined exactly. DFT benchmarks⁶ of this energy
99 contribution are imprecise for 11 much-used functionals.

100 Recently, however, several new DFT functionals have
101 emerged that improve performance compared to calorimetric
102 measurements of adsorption energies. Hence, DFT is very
103 informative, for example, on nanostructured substrates and
104 kinetics (combined with kinetic Monte Carlo).^{7–9}

105 QMC benchmarks for hydrogen dissociation on Cu(111)
106 and other metals compared to molecular beam results are
107 available with an accuracy of 1–5 kJ/mol (with progress in
108 controlling statistical or standard error [se] and systematic
109 error), see ref 10.

110 Hence, this theoretical study develops a novel QMC
111 methodology for water addition to preadsorbed carbon
112 monoxide in a hollow site in the Pt(111) plane of the catalyst.
113 The results below give the relevant transition-state geometry
114 obtained with QMC force constants. The corresponding
115 activation barrier is the energy difference for this TS (at the
116 energy maximum for water addition) compared to that of
117 adsorbed CO at Pt(111) with water at 8 Å. Subtracting
118 ground-state energy from the QMC results for these two
119 geometries enables us to achieve remarkable accuracy for this
120 activation barrier. The QMC activation energy that results has
121 error bars below 1 kJ/mol. Therefore, it is close to measured
122 apparent activation energy values and well within 95%
123 confidence limits.

124 ■ COMPUTATIONAL METHOD

125 The method of choice must scale well with system size, be able
126 to efficiently use modern supercomputer facilities that are
127 massively parallel and, above all, produce quantitative, accurate
128 physical properties that are difficult to obtain otherwise. QMC

benchmarks of activation barriers for reactions adsorbed on
solid catalyst surfaces fit this description well. Developing and
applying QMC calculations on this scale require access to a
super computer.

Stages of Our Approach are as Follows.

- 1 An active site is defined with 2 Pt-atoms. Pt₁ receives H,
and Pt₂ defines an equilateral triangle motif (with
translation symmetry) in the (111) face and a hollow
site at this triangle's center of mass, where CO is
adsorbed: the atoms involved are Pt₁, Pt₂, CO, and H₂O.

Active site coordinates in a.u. for TS input geometry from
QMC force constants (below).

- 2 MOLPRO¹¹ uses this input to evaluate a MRCI wave
function, which is embedded in the Pt-lattice with a 2 ×
2 atom face and five (ABCBA) layers. This defines a
periodic slab. The “active site” embedded in Pt-slab
(without Pt-atom duplication) is expanded in plane
waves, with periodic boundary conditions in k-space.

atom	x	Y	z
Pt ₁	0.0000	0.0000	0.0000
Pt ₂	2.6137	4.5271	0.0000
C	2.6137	3.0179	4.3000
O	2.6137	4.4344	6.5864
O	1.9000	0.0000	4.3000
H	0.0000	0.0000	3.0500
H	1.3155	0.0000	6.0126

Embedding simply uses standard Green matrix addition for
the electronic potential.¹²

- 3 The Slater determinants obtained from this wave
function are expressed as products with a generic
Jastrow factor that is in Slater–Jastrow form, giving a
trial wave function (TWF). QMC proceeds in two steps:
variational and diffusion Monte Carlo or VMC and
DMC.
- 4 The TWF with arbitrary parameters (polynomial
coefficients of interparticle distances in the Jastrow
factor and Slater determinant weights) are optimized
using VMC.
- 5 Then, diffusion Monte Carlo (DMC) uses a population
of “walkers” (instantaneous particle positions) generated
from the optimal TWF, propagated in imaginary time.

DMC and DFT-MRCI methods, when compared, give
percentage errors of 3% for DFT-MRCI and only 0.4% for
DMC in total excitation energies for systems of similar size.¹³

A simple model of the catalyst surface (planar, no steps,
terraces, or defects) is retained. This shows that even the
nanostructuring of the real surface and an excellent agreement
between the apparent activation energy and the value
calculated using QMC (for a planar surface) are compatible.
The energy is referenced to that of adsorbed CO, in its
optimized geometry. It is based on a transition state for water
addition without complete dissociation. This work treats
among the largest heterogeneous systems studied by QMC
with a metal surface and adsorbed interacting molecules. The
forward water–gas shift reaction is greatly facilitated on the
Pt(111) catalyst giving hydrogen. The first step is water and
preadsorbed CO addition, studied here at Pt(111).

CASINO software¹⁴ is used. It cannot be treated as a “black
box” for these applications.

The electrophilic CO carbon is in a hollow site near three
equivalent Pt-atoms (see above). One Pt atom thus accounts

for all three, as the key to embedding a high-level wave function for a relatively small active site containing only the two “distinct” Pt-atoms. One begins binding to the H-atom of the stretched water bond and defines our origin and the other defines the triangle within which the hollow site adsorbing CO is situated.

A QMC saddle point or energy maximum on this reaction path step gives us TS geometry.

The TS is shown in Figure 1 (TS1). The water oxygen binds to the (CO) carbon, while the hydrogen from the stretched O–H binds to a vicinal Pt-atom. The activation energy obtained from TS1 is significantly lower than that for water dissociation. TS1 has a slightly short CO bond because some electron density involved in beginning the bonding with the water oxygen comes from a CO antibonding orbital. The water

molecule has a very long OH-bond (1.2 Å), its hydrogen binding to Pt at (0,0,0). The other OH is almost unchanged.

For water dissociation on Pt(111), our previous QMC calculation gave (in kJ/mol) 74.27 (with se 1.3) compared to a DFT value of 75.32.

The present TS gives a significantly lower barrier of 71.0 (se 0.7). Any OH radicals first bind to a surface platinum atom. Hence, diffusion of these “bound” hydroxides is difficult.⁵

Se is evaluated from the raw QMC data, after the equilibration phase. Twist-averaging is used to markedly lower the se. It requires a new run for each offset grid and removal of equilibration data points and then extrapolating to the small time-step limit.¹⁴ This gives error bars of these activation barriers that are much lower than in our QMC benchmarks for Cu(111).¹⁰ Because of the 3d electrons, hydrogen dissociation barriers at Cu(111) had statistical error slightly above chemical accuracy (*i.e.*, 1 kcal/mol or 4 kJ/mol).

Water dissociation before attack of CO can be eliminated in favor of a concerted (partial) dissociation accompanied by attack of CO by barrier differences and low error, as seen on Pt(111), but this would not have been possible for error bars obtained with the copper catalyst, using the QMC calculations of ref 10. Some indications on possible improvements were discussed in ref 10. These studies provided useful indications on the tendencies. Extrapolation to the basis set limit in plane waves indicates that the QMC barrier is an upper bound on the actual value and, generally, it was rather lower than accurate molecular beam measurements. This trend explains why the measured value (which may be lower because of defect sites for reaction) agrees with the QMC value well (that has been seen to give values below those measured).

In fact, 95% confidence limits are within 1.4 kJ/mol and this shows a modest effect of statistical error and the significantly higher water dissociation barrier (3.2 kJ/mol greater).

Hence, QMC methods described here represent a breakthrough in reliable information on bond-dissociation limitation of metal-catalyzed reactions.

Methodological advances requiring built-in benchmark work are given here.

For details of computational results, see the Supporting Information and also the figshare.com/articles/dataset.^{1,15}

Platinum has a 5d⁹ 6s¹ ground state. Because all-electron calculations are inaccessible, a Pt-atom is represented by 18 valence electrons with a suitable PP. Core–valence occupation is low in any given region of space: related densities are well-separated. This confers low variance on the metal wave function, only about 10% of that for problematic copper metal wave functions. The platinum PPs used gives reliable excitation energies.¹⁶

Basis and PP will influence accuracy for adsorption by metals. Plane waves with a complex exponent allow basis sets to include Slater type orbitals, which facilitates embedding.^{17,18}

In the present work, the CASINO QMC code is used. The force constant algorithm therein¹⁹ gave a molecular active site in a Slater-type orbital basis for the TS, expanded in plane waves like the periodic solid (extending our previous work^{18,20}).

Transferrable atomic core electrons must be replaced by effective core potentials or PPs. For QMC, norm-conserving PPs are needed. Core electrons account for nearly all the total correlation energy.²¹ With suitable PPs (see Supporting Information), electron correlation contributions approach the all-electron limit. PP nonlocality can cause havoc, if the core is

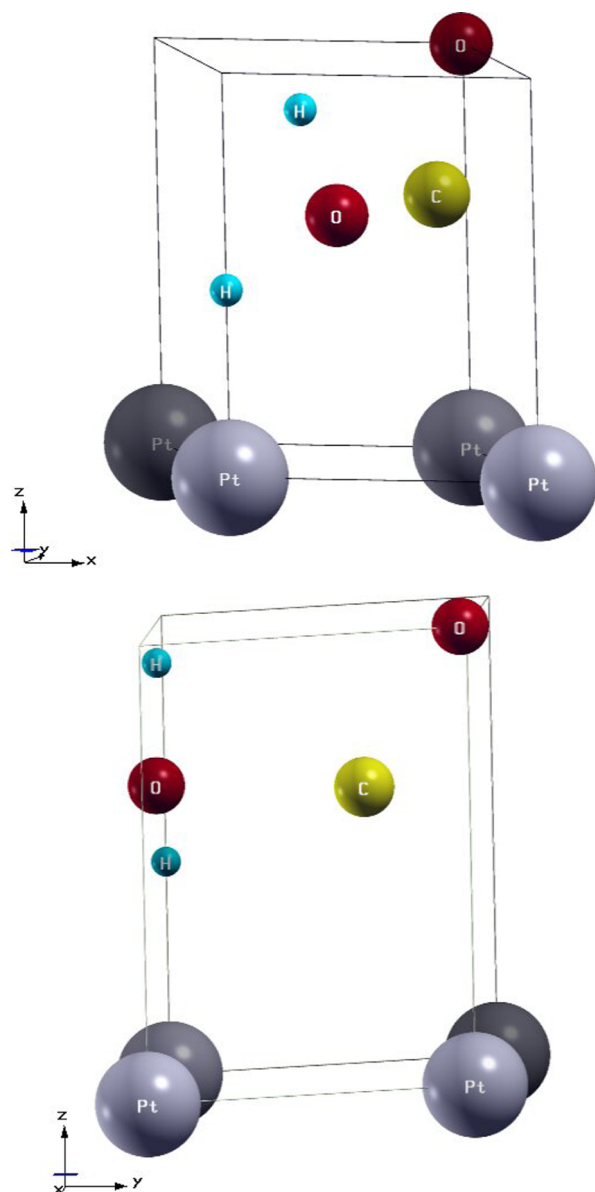


Figure 1. Molecular active site (TS) TS1: the $z = 0$ plane is the Pt(111) surface (bottom face). Pt at the origin accepts one water H-atom. CO carbon in a hollow site (Pt–C bond-length 1.43 Å), the oxygen is above a vicinal Pt. Water (oxygen) O–C distance is 1.63 Å. Top pane: from negative y. Bottom pane: from positive x.

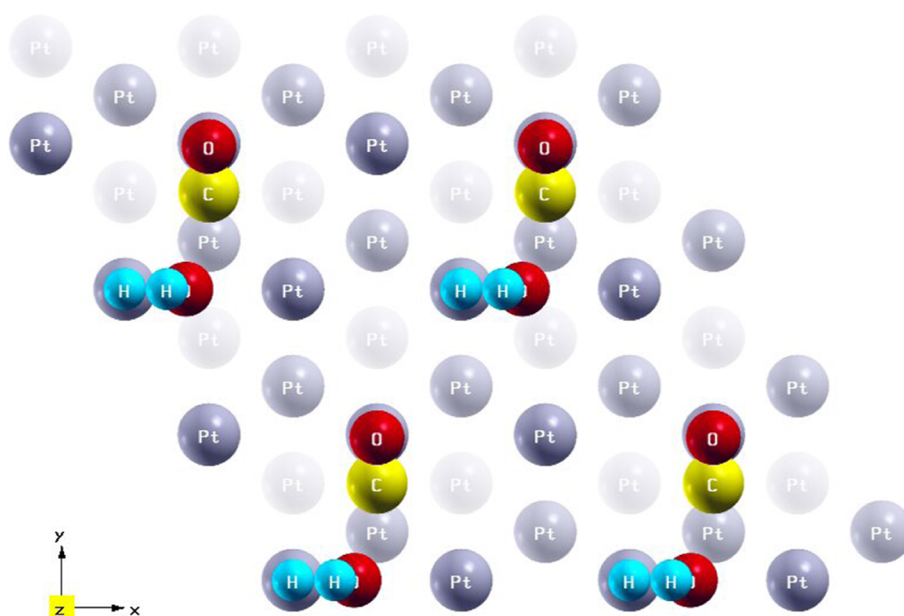


Figure 2. Molecular active site (TS): the $z = 0$ plane is the Pt(111) surface (bottom face). Top view of all four cells corresponding to Figure 1 in the $2 \times 2 \times 1$ coordinate-space expansion.

too large or a poor choice of local channel (l -value) is made, especially for elements with valence 3d shells; see ref 22. The 4d and 5d are 10 times lower in variance, ascribed to the lower dispersion of the electron distributions, for increasing effective atomic charge.

QMC METHOD: SPECIFICATIONS

The present study underpins heterogeneous catalysis that enhances bond dissociation. This step is frequently the initial (and often limiting) step of an industrial reaction (see, e.g., refs 23 and 24). Bond dissociation is difficult to describe using Hartree–Fock (HF) approaches.

HF methods in fact give incorrect dissociation products. This is even for homonuclear diatomics. However, extensive CI caters for electron correlation adequately (but limits the size of accessible systems). DFT methods are a rapid computational alternative.

DFT includes some electron correlations and performs better than HF in the dissociation limit for certain functionals. The Perdew, Burke, Ernzerhof (PBE) functional (reproducing experimental lattice parameters accurately) gives a reasonable gas-phase barrier for ammonia synthesis.²⁵ The initial QMC trial wave function should have precise nodes if possible, in particular close to dissociation. A high-level wave function²⁶ embedded in periodic Kohn–Sham PBE plane-waves is a suitable starting point for QMC work on transition-metal systems.

This work uses the QMC method that proceeds in a variational (VMC) then diffusion (DMC) stage. DMC includes almost all the correlation energy and is suited to bond dissociation.

The QMC approach uses statistical physics over a large population, comprising sets of instantaneous particle positions in co-ordinate space (or configurations). They are often called “walkers” (cf. the one-dimensional random-walk). “Walkers” are chosen randomly giving initial electron density of the trial wave function.

After equilibration, many data points N give error decreasing as $1/\sqrt{N}$. Trial wave function quality is carefully optimized. Finite size effects are catered for. Solid-state QMC scales slowly with system size (n electrons scale as n^3), using a cubic spline (blips)²⁷ basis.

The purpose of the work reported here is to study the stabler of two possible catalytic reaction paths for water addition to preadsorbed CO, distinguished via their specific TS.

The statistical error (0.7 kJ/mol) on the mean calculated reaction barrier heights does not include specific systematic contributions (because of nonlocality of the PP and poor nodes of the trial wave function). We strive to limit them here.

We found that water addition to CO preadsorbed on Pt(111) can occur in two ways:⁴

I a step-by-step process, with rate-limiting water dissociation on Pt.²⁸

II a concerted step, with CO and water coordinated to the metal.

We have excluded pathway I above. Hence, we consider pathway II: QMC energies of asymptotic physisorbed geometries for CO and H₂O are subtracted from that of the stringently optimized QMC geometry for the adsorbed transition state (TS).

The TS geometry results from the Hessian with QMC force constants as matrix elements. (The matrix is updated using Pulay’s direct inversion in the iterative subspace (DIIS) algorithm adapted by Farkas²⁹). Hence, the TS geometry uses optimization guided by QMC force constants and permits precise evaluation of the activation barrier height.

Setting up the Model System. Figure 2 is a view from above the periodic cell used in this work, with adsorbed molecules and using translational symmetry. The dark gray Pt atoms define unique positions in a planar (111) surface at $z = 0$. A five-layer Pt-slab is defined (80 atoms), and a Generic Jastrow factor is used for all distinct atoms, that is, each atom of water, carbon monoxide, and surface and bulk Pt-atoms (surface Pt atom types may also be distinguished by adsorbate

interactions). The geometry (Figure S1, coordinates in the Supporting Information) serves as QMC transition-state input. Finite-size effects are reduced on a large grid: a 3 3 1 grid defines the largest accessible real-space super-cell, much smaller than that converged in DFT/plane waves (RAM limit). The DFT calculations converge only at 16 16 1 or higher. They are useful as the control variate in twist-averaging. This corrects for finite size error which cancels between asymptotic and transition-state geometries leaving below 1/10 of the error. Runs on a 2 2 1 grid reduced finite size error by a factor of 25 (127 for 3 3 1) compared to a gamma-point calculation. Semicore electrons are required but have much less influence on metallic systems conserving the number of metal atoms in very similar geometries (bulk metal atoms are almost bystanders). Comparing asymptote and QMC optimized TS geometries for reaction barriers is such a case. Coordination of the TS to the metal surface occurs, but the distance between atoms is at most 40% more than the equilibrium bond-length and referring to unstretched bonds little affects semicore electrons. A $Z = 60$ core for Pt is validated below.³⁰

RESULTS

Validating PPs for a Simple Test Reaction of Platinum. Previous work used Troullier Martins norm-conserving PPs (TMPP). The core size (68) was too large to accurately monitor the reaction: $\text{Pt}_2 + \text{H}_2 \rightarrow 2\text{PtH}$.

This work converts the ECP used in MOLPRO for the active-site molecular wave function to a norm-conserving form which has the same local channel as ECP60MDF.³⁰

The above PtH formation reaction tests both the PP and performance of DMC options used in these QMC calculations. Numerical integrals over these choices of PP (with Casula T-moves to correct for nonlocality³¹) use finite expansion order and limiting accuracy. The TMPP is relatively hard, conferring low variance on the wave function. Variance is further reduced using the ECP60MDF.

Test calculations refer to $\text{Pt} + \text{H}_2$ (giving PtH_2 (a) and $\text{Pt}_2 + \text{H}_2$ giving 2 Pt-H (b)).

Activation for (b) that has been shown to proceed *via* a squarish/rectangular TS with the TMPP gave a QMC value of 21 kJ/mol above that from reference multireference single and double CI (MRSDCI) calculations of 61 kJ/mol.³²

For $\text{Pt}_2 + \text{H}_2$, a binding energy of 147.4 kJ/mol is obtained with a TMPP by QMC. A value of 128.5 kJ/mol is obtained from MRSDCI benchmarks.³² This major discrepancy shows residual local approximation errors in the TMPP, prohibiting its use in the Pt(111) work.

Hence, we adapted a hard PP (with 18 electrons treated explicitly).

The PP used is MDF60PP³⁰ (8 of the 4f electrons are included, as valence, with the electronic ground-state ($5d^9 6s^1$); see Supporting Information); it was found to permit accurate evaluation of the test reaction energies. The QMC binding energy was 130.2 (*c.f.* MRSDCI 128.5) kJ/mol³² with an se of 2.1 kJ/mol. The activation barrier was 62 within 2.5 kJ/mol.

These results confirm the accuracy of our approach, using a trial wave function from MOLPRO for molecular systems. These reacting systems are embedded in a periodic cell.

Use of QMC to Describe $\text{CO} + \text{H}_2\text{O}$ Adsorbed on a Pt(111) Surface. Molecules interact with both the periodic surface and each other. A slab construct, limited by relaxed

Pt(111) (reaching the experimental bulk geometry in four layers) is used.

Carbon monoxide (CO) adsorption is at a hollow site of Pt(111), denoted CO_{ads} . Carbon monoxide gas is rather inert. The carbon atom has a small partial negative charge.

The strong bonding of gaseous CO molecules is weakened during adsorption, and its polarity is reversed by Pt–C interactions at Pt(111), facilitating its attack by water.

structure	clean Pt(111)	Pt(111) CO_{ads}	CO	H_2O
E_{tot} (Ha)	−511.792	−533.448	−21.517	−16.210

Reference QMC calculations (in Hartree cf Table 1 below). 413 t1

Table 1. Activation Energy Evaluation for Online Data Sets from this Work¹⁵

structure	transition state	asymptote
E_{tot} (Ha)	−549.63223	−549.65924
variance a.u./(kJ/mol) ² : se kJ/mol	0.507/3.5: 1.87*	0.528/3.64: 1.91*

It was found to be more accurate to refer the CO_{ads} geometry with a physisorbed incoming water molecule (asymptote of Table 1) to evaluate activation barriers.

Investigation of this phenomenon has been carried out using infrared reactor cells (*in situ* FTIR,³³) at a number of solid surfaces. Here, we give QMC results for its reaction with water. Removal of toxic carbon monoxide molecules is a typical depollution reaction, of interest for catalytic exhausts. Furthermore, the reaction with water is of industrial importance in producing clean fuels (hydrogen gas) in a sustainable process. In earlier work,^{20,33} it was shown that the stretch frequency of carbon monoxide makes it a highly sensitive probe to surface interactions. This frequency is a measure of adsorption. The carbon monoxide bond length is just below 120 pm. It is now a carbonyl group that is the site of the nucleophilic attack.

CO and Water Addition on Pt(111) Investigated Here. Water reacts with preadsorbed CO, as shown by preliminary DFT (PBE) investigations.

Final reaction products are CO_2 and gaseous hydrogen (fuel restoring water as the combustion product). CO adsorbed on Pt(111) was optimized using QMC force constants.

The C–O bond length was found to be 118 pm, only slightly longer than the gas-phase value of 113 pm, with water interaction depleting CO antibonding electron density.

From FTIR work on CO ,³³ the dipole implies a partial positive charge on carbon (evaluated by QMC at +0.098e), ready for water attack. The Pt–C distance is 2.28 Å.

Water dissociation concerted with oxygen binding to the CO carbon is rate-limiting.

In Figure 1, (see the above model section) we show the present QMC geometry of the TS. Water with the leaving $\text{H}^{\delta+}$ binds with a surface Pt-atom, while the remaining O–H forms a V-shaped $\text{H}-\text{O}^{\delta-}-\text{C}^{\delta+}=\text{O}$ intermediate. The CO carbon atom and H_2O oxygen are 2.27 Å above the Pt(111) face. QMC-optimized geometry yields three Pt–C bonds: 2.28 Å.

The O–C linkage forming is still 1.63 Å long (in this TS). The four-Pt atom skin lozenges are at the apices of a trigonal (*i.e.*, hexagonal) close-packed cell with a Pt–Pt distance of 2.783 Å.

DMC energy calculations for the TS and asymptote geometries, after averaging 16 stochastically generated twists

for each geometry using the CASINO/pwscf interface for I or II:

I water dissociation at Pt(111): QMC barrier of 74.27 (se is 1.3 kJ/mol). This is in good agreement with PW91 Ultrasoft (USPP) values: 75.32 kJ/mol.²⁸

N.B. gas-phase water dissociation has a barrier above 492 kJ/mol.

II water dissociation concerted with the start of the nucleophilic attack of CO at Pt(111): QMC study based on the TS of Figure 1 above, in the Model section [with the carbonyl polarization of adsorbed CO, *i.e.*, partial positive charge on carbon unlike CO (gas)]. Some mechanistic studies of the water–gas-shift reaction^{28,34} have suggested that water dissociation is rate-limiting and followed by attack of CO (I). This scenario was studied and found to be less favorable in.⁴ A concerted TS (II) illustrated in Figure 1 is determined here.

Concerted addition II is validated in this work. It has also previously been postulated.⁵

The repository data set¹⁵ for the given k-points in the first Brillouin zone defined for the transition state and referred to the asymptote give the tabulated values below:

Tabulated values are for the DMC population target weight. Activation barrier: 0.02701 a.u. or 70.96 (5) ± 2.7 kJ/mol, (using *) showing a comparable se value in kJ/mol for TS and asymptotic gamma point distributions, which validates our MRCI input. The se is reduced by a factor of 4 by twist-averaging (combining runs from 16 offset grids in the first Brillouin zone) to under 0.7 kJ/mol (see the Supporting Information).

The final QMC barrier is 71.0 with an se of 0.7 kJ/mol. This QMC value could be taken as a lower bound for the activation barrier, limited by the activated complex. The actual system will depend on temperature, surface rearrangement, and possible defects. Agreement is perfect with this model: apparent activation energy measured is 71.4 kJ/mol.

PERSPECTIVES AND CONCLUSIONS

This QMC determination of the transition-state structure and reaction barrier height for water addition to CO preadsorbed on a close-packed platinum Pt(111) plane corresponds well to measured apparent activation energy. It is accurate to 1 kJ/mol. The so-called chemical accuracy is over four times less stringent. A concerted water-stretch and addition step is favored (see Figure 1). Water dissociation giving OH-radicals is excluded by their adsorbed and activation of bond-breaking before addition to CO is 3 kJ/mol higher. The platinum metal surface is studied. A small molecular structure, described by an MRCI Slater determinant that is optimized using QMC forces and the CASINO software, is embedded in plane waves.

A DFT calculation of the Pt-slab structure yields Kohn–Sham PBE orbitals. They define the trial QMC wave function, combined with a generic Jastrow factor. This embedding procedure is validated for hydrogen dissociation on platinum³⁵ (testing the Pt(111) slab used here). The trial wave function thus shows accurate nodes, limiting barrier height systematic errors. A statistical (standard) error of 0.7 kJ/mol reflects total error, close to that of measured apparent activation energy.

A truncated CI was used here (20–100 determinants); however many configurations of small but similar weight may have an influence and have so far been neglected. Perspectives

for extending this strategy use compact molecular full-CI input available from NECI.²⁶

Pt-atoms form an equilateral triangle in the Pt(111) plane. A unique Pt-atom defined using translational symmetry represents all three. We refer to CO adsorbed above the centroid.

This gives three C–Pt linkages. The data giving the TS structure uses CASINO QMC force code and a contact molecule, comprising CO + H₂O and a monolayer of Pt(111) optimized using QMC and placed on the slab at the experimental spacing. The size and complexity of this system require considerable supercomputer resources.

VARIATION AND DIFFUSION QMC

Variation Monte Carlo. A preliminary Variational Monte Carlo (VMC) calculation is carried out generating several thousand configurations (“walkers”: instantaneous points in electron coordinates) to sample electron density. In VMC driven by energy minimization, the local energy: H_ψ/ψ is minimized. The product of a Jastrow factor with a Slater determinant gives the trial wave function. The Jastrow factor includes electron pair, electron nucleus, and three-body (two-electron and nucleus). This Jastrow factor^{36,37} is carefully optimized (requiring 5% of the total time). This factor uses a polynomial expansion in the variables of explicit correlation.

Generic Jastrow Factor. Defining a Slater–Jastrow wave function as the product of Ψ_S , a Slater determinant, and the exponential with, as argument, an explicit correlation Jastrow factor $J(R)$:

$$\Psi(R) = e^{J(R)}\Psi_S(R) = e^{J(R)}D_u(R_u)D_d(R_d) \quad (1)$$

The determinants $D_u(R_u)$ and $D_d(R_d)$ treat “up” and “down” spin separately if necessary. This new approach³⁷ generates a large parameter set that was tested for our platinum slab model, which is presented above.

The generic Jastrow factor used had e–e, e–n, and e–e–n polynomials expanded to ninth order, truncated to a finite range (around 10 a.u.) with the factor: $t(R) = (r - L)^C \Theta_H(r - L)$; Usually $C = 3$, because the wave function and at least the first two derivatives are continuous.

Θ_H is the Heaviside function and L is the range, for example, Wigner–Seitz cell diameter.

$$J(R) = \sum_{i < j}^N u_{p_{ij}}(r_{ij}) + \sum_i^N \sum_I^{N_n} \chi_{S_{il}}(r_{il}) + \sum_{i < j}^N \sum_I^{N_n} f_{T_{ijt}}(r_{il}, r_{jl}, r_{ij}) \quad (2)$$

where u , χ , and f are parameterized (polynomial) functions in the interparticle distances.

The symbols P, S, and T denote the pair, single, and three-particle channel indices.

The u term caters for interelectron contributions over r_{ij} and the χ term is for electron–nuclear terms over r_{il} . They are both constructed to obey Kato’s cusp conditions.

The f term is the three-particle electron pair and nucleus contribution that cannot be neglected. It is expanded over r_{ij} and two r_{il} variables.

This Jastrow factor (in common algebraic specification language) is fully optimized during the VMC step. It contains many polynomial coefficients, as variational parameters, offering flexibility. The parameter set structure used for

571 optimization in TS and asymptotic geometry generic Jastrow
572 factors are given in the [Supporting Information](#).

573 The electron distribution is updated until the final stages of
574 VMC, where fine-tuning of the Jastrow factor is accomplished
575 by energy minimization over 15 cycles. Our fully-optimized
576 generic Jastrow factor is given in the online repository.¹⁵

577 The resulting Slater–Jastrow wave function is used to
578 initialize the configurations for diffusion Monte Carlo (DMC).
579 This gives prohibitively long DMC cycles.

580 Three parameter sets result for all 25 atoms in the super-cell,
581 treated individually. It is close to the variational energy
582 minimum for the system defined: (−448.32 Ha, with the PP
583 from the ECP ECP60MDF with $l = 1$ as the local channel).³⁰

584 DMC cycle duration is cut down by maintaining individual
585 parameter sets only for atoms in molecular species (CO and
586 water). The platinum atoms are grouped according to rules for
587 surface and bulk atoms (using translation symmetry). These
588 rules allow us to use a single parameter set for each of the
589 interparticle terms for each group.

590 A Jastrow factor is optimal in a given parameter set for these
591 rules, giving a minimum energy slightly above the variational
592 limit. It is therefore of paramount important to conserve the
593 same rules for definition of the generic Jastrow factor in each of
594 the limiting geometries (TS and asymptote). The same atoms
595 are involved but with some “bonding” surface interaction for
596 the TS and very little interaction for the asymptote. The
597 correlation space spanned by the parameter sets used is
598 conserved in the present work. When generic Jastrow
599 optimization has reached a stable minimum, a final VMC
600 calculation generates the initial configurations required for the
601 diffusion Monte Carlo step (DMC); 10–20 per core. The
602 previous VMC steps must generate at least as many
603 configurations.

604 **Diffusion Monte Carlo.** In the DMC method, the ground-
605 state component of the trial wave function is projected out by
606 solving the Schrödinger equation (SWE) in imaginary time.
607 DMC is carried out in the fixed-phase approximation, which
608 uses the nodes from the input trial wave function.

609 An updated overview of the VMC and DMC methods is
610 given in ref 14. These trial wave functions can be optimized
611 with a complex Jastrow factor,³⁸ because they potentially
612 provide the input with exact nodes. This improves the single
613 Slater determinant describing a ground state from the DFT
614 orbitals for heterogeneous systems. DFT nodes may well be
615 poor. The nodes are improved by embedding the MRCI active
616 site.

617 The time-dependent Schrödinger equation (TDSWE) is
618 transformed into a diffusion equation in the 3N-dimensional
619 space of electron coordinates (with the potential energy acting
620 as a source/sink term) by replacing t by the pure-imaginary
621 time it , in this TDSWE:

$$622 \quad i \frac{d}{dt} \Psi(\mathbf{r}, t) = -\frac{1}{2} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}) \Psi(\mathbf{r}, t) \quad (3)$$

623 where ∇^2 is the scalar Laplacian of an instantaneous electron-
624 position vector: $\mathbf{r}$.

625 Defining the Hamiltonian (for stationary states):

$$626 \quad \mathcal{H} = -\frac{1}{2} \nabla^2 + V(\mathbf{r}) \quad (4)$$

627 As outlined above in eq 2, the time-dependent SWE
628 (replacing it with τ) becomes the diffusion eq 4 below. Excited
629 state density contributions contain exponentially decreasing

factors, fading out as the “time” variable $\tau = it$ is increased in
many small steps.

The best-estimate of the ground-state energy eigenvalue
(E_0) is adjusted. Note that the exact value gives a zero
derivative. This is solved combining diffusion and branching or
dying processes.

$$-\frac{d}{d\tau} \Psi(\mathbf{r}, \tau) = (\mathcal{H} - E_0) \Psi(\mathbf{r}, \tau) \quad (5)$$

Introducing importance sampling, using the trial wave
function transforms the problem into one involving drift as
well as diffusion but greatly reduces the population fluctuations
because of the branching/dying process. The Fermionic wave
function antisymmetry is maintained by constraining the nodal
surface equal to that of the trial wave function.

To resolve energy values, QMC statistical error in total
values must be relatively small.

When the cost of the equilibration phase of a QMC
calculation is negligible, $\sigma = k/T$, where σ is the se. Accuracy
for a given time hence also depends on the quality (nodes) of
the trial wave function. Lower fixed-phase error reduces the
equilibration time.

The DMC algorithm proceeds using Casula T-moves³¹ and
a time-step of 0.005 a.u. These are continued until the error in
se is 0.1, that is, for 30,000 data points on average for 16 twists
(requiring complex wave functions as for our structure with no
inversion center).

■ APPENDIX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at
<https://pubs.acs.org/doi/10.1021/acs.jpcc.0c07304>.

Trial wave function and PP, periodic super-cell
(definition and atom coordinates), limiting possible
systematic error in QMC, CASINO software version,
and generic Jastrow factor structure and definition rules
(PDF)
(PDF)

■ AUTHOR INFORMATION

Corresponding Author

Philip E. Hoggan – Institut Pascal, Aubiere Cedex 63178,
France; orcid.org/0000-0002-2543-5823; Phone: +33 (0)
4 7340 5170; Email: philip.hoggan@uca.fr; Fax: +33 (0) 4
7340 7340

Authors

Rajesh O. Sharma – Institut Pascal, Aubiere Cedex 63178,
France
Tapio T. Rantala – Physics Department, Tampere University,
Tampere 33014, Finland

Complete contact information is available at:
<https://pubs.acs.org/doi/10.1021/acs.jpcc.0c07304>

Notes

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