A coming of age for many-body methods: Achieving consensus with experiments for CO on MgO

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Abstract

The adsorption energy of a molecule onto the surface of a material underpins a wide array of applications, spanning heterogeneous catalysis, gas storage and many more. It is the key quantity where experimental measurements and theoretical calculations meet, with agreement being necessary for reliable predictions of reaction rates and mechanisms. The prototypical molecule-surface system is CO adsorbed on MgO, but despite intense scrutiny from theory and experiment, there is still no consensus on its adsorption energy. In particular, the large cost of accurate many-body methods makes reaching converged theoretical estimates difficult, generating a wide range of values. In this work, we address this challenge, leveraging the latest advances in diffusion Monte Carlo (DMC) and coupled cluster theory [CCSD(T)], to obtain accurate predictions for CO on MgO. These reliable theoretical estimates allow us to evaluate the inconsistencies in published temperature programmed desorption experiments, revealing that they arise from variations in employed pre-exponential factors. Utilizing this insight, we derive new experimental estimates of the (electronic) adsorption energy with a (more) precise pre-exponential factor. As a culmination of all this effort, we are able to reach consensus between multiple theoretical calculations and multiple experiments for the first time. In addition, we show that our recently developed cluster-based CCSD(T) approach provides a low cost route towards achieving accurate adsorption energies. This sets the stage for affordable and reliable theoretical predictions of reaction mechanisms and rates to guide the realization of new catalysts and gas storage materials.

Introduction

The adsorption energy (E_{ads}) of a molecule onto the surface of a material is a quantity of fundamental importance. For example, adsorption (or desorption) forms the primary rate-limiting step of many critical reactions in heterogeneous catalysis,[1,2] with overall reaction rates determined by their E_{ads}.[3,4] It is also used to determine the selectivity of a surface for binding a particular molecule, relevant for the storage and sequestration of gases pertinent to energy applications.[5] These properties depend sensitively on the value of E_{ads} and it is of vital importance that it can be determined accurately, either with theoretical calculations or experimental measurements.

Touted as the 'hydrogen molecule of surface science',[6] the CO adsorption energy onto the MgO (001) surface has served as the quintessential test for both theory and experiment.[7–14] It is highly representative of many important processes (e.g., CO oxidation[15] and N_2 reduction[16] in surface catalysis, as well as CO_2[17] adsorption in gas storage) and the weak van der Waals (vdW) dispersion interactions that govern the E_{ads} makes it a stringent test. As such, a method incapable of obtaining the E_{ads} of CO on MgO accurately cannot be trusted to reliably predict molecule-surface interactions for more complex surface phenomena. In this context, an E_{ads} prediction is typically considered reliable if it reaches "chemical accuracy" of 43 meV (1 kcal/mol).[18] This level of precision on E_{ads} (together with smaller entropic together) is essential for the dependable estimation of crucial thermodynamic properties, including chemical reaction rates.[19]

Unfortunately, obtaining an accurate E_{ads} is highly challenging for both theory and experiment. Despite a large body of experimental and theoretical investigations (Fig. 1a), the E_{ads} of CO on MgO is still under debate. Even nominally accurate many-body theoretical methods (Fig. 1a) can produce a range of nearly 500 meV (12 kcal/mol) on E_{ads}, encompassing predictions going from weak physisorption to moderate chemisorption. At room temperature, this range can lead to over 8 orders of change in reaction rate predictions. Experimental measurements have covered a similar range in the past[11–14] and while recent estimates (Fig. 1a) have settled to between −133 and −208 meV , this range is still too large. Crucially, it has not been possible to establish agreement on the CO on MgO E_{ads} between multiple theoretical approaches and multiple experiments at the same time (see Sec. S1.2 of the Supporting Information).

Modeling the weak vdW interactions that govern CO on MgO binding requires a rigorous treatment of its electronic structure. This raises question marks over common electronic

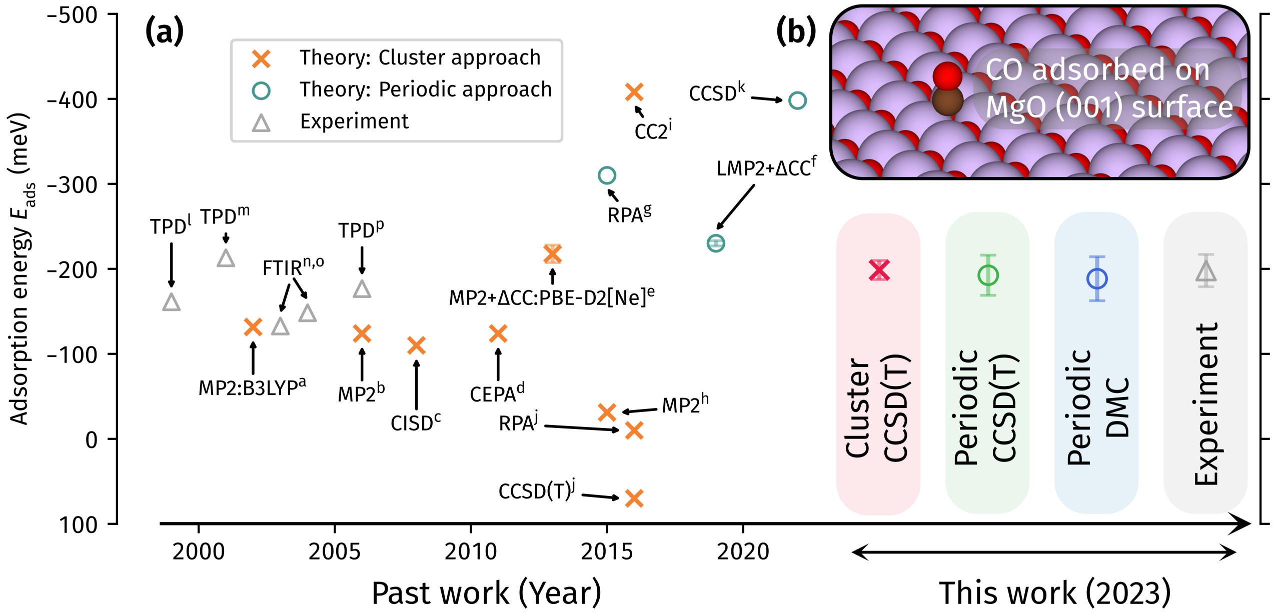

Figure 1: (a) Adsorption energy E_{ads} of CO on MgO from past experimental and theoretical investigations. For the past theory work, we focus on many-body wave-function studies employing either a cluster or periodic approach. The past experimental work involves either the Fourier transform infrared (FTIR) or the temperature programmed desorption (TPD) technique, which we discuss in Sec. S9 of the Supporting Information. The CO on MgO system is visualized in the top panel of (b) and in its bottom panel, we give accurate estimates to E_{ads} from this work utilizing CCSD(T) with a cluster approach, CCSD(T) with a periodic approach and DMC with a periodic approach. A best estimate to the experimental value has also been made by reanalyzing the previous experimental work with an improved pre-exponential factor (discussed in the text). Error bars have been determined for all estimates made from this work. References for past simulation work are as follows: [a]Ugliengo *et al.*[20] [b]Herschend *et al.*[21] [c]Qin *et al.*[22] [d]Staemmler[23] [e]Boese *et al.*[24] [f]Alessio *et al.*[25] [g]Bajdich *et al.*[26] [h]Li *et al.*[27] [i]Heuser *et al.*[28] [j]Mazheika and Levchenko[29] [k]Mitra *et al.*[30] References for past experiments are as follows: [l]Wichtendahl *et al.*[31] [m]Dohnálek *et al.*[32] [n]Spoto *et al.*[33] [o]Spoto *et al.*[34] [p]Sterrer *et al.*[35]

structure methods, such as density functional theory (DFT) or second-order Møller Plesset perturbation theory (MP2). The former does not naturally incorporate vdW dispersion in its standard approximations (although approaches[36–38] are available), while the latter lacks higher-order dispersion effects.[39] Moreover, it is not clear whether established many-body methods, in this case quantum diffusion Monte Carlo (DMC)[40] and coupled cluster with single, double and perturbative triple particle-hole excitation operators [CCSD(T)],[41] are necessarily accurate for surface-molecule adsorption. For example, while model surfaces have been previously studied by DMC[42–47] and CCSD(T),[48–52] sometimes successfully in conjunction,[46,53,54] recent work[55] has indicated significant differences for the interaction energies of large and complex molecules.

Applying DMC or CCSD(T) to surface problems is highly challenging because of the steep scaling of their computational complexity with the number of atoms. With these methods, surfaces can be modeled either as a finite cluster or a repeating supercell slab, termed cluster and periodic approaches respectively. To date, neither DMC nor CCSD(T) have been applied to examine CO adsorption on MgO with a periodic approach. While CCSD(T) with a cluster approach, termed cluster CCSD(T) hereafter, has been previously performed, it is difficult to converge. For example, the aforementioned 500 meV range arises from cluster CC-based E_{ads} estimates that are not adequately converged. Here, the challenge lies in simultaneously converging both the surface model (size) and electronic structure settings. The former requires large system sizes (both cluster and periodic) to reach the bulk (infinite size) limit and a dilute CO coverage, while the latter requires large basis sets and the inclusion of correlation from electrons in sub-valence metal shells. These requirements all contribute to a significant computational burden that can readily become intractable.

In this work, we reach a consensus for the CO on MgO E_{ads}, achieving agreement between theory and experiment. For theory, we leverage the latest advances in periodic DMC, periodic CCSD(T), and cluster CCSD(T) to produce three high-quality estimates of the E_{ads}. With this, we establish agreement between all three theoretical techniques to sub-chemical accuracy. This has allowed us to evaluate and understand the inconsistencies in previous theoretical calculations and experimental measurements. For example, we establish that the discrepancies among previous temperature programmed desorption (TPD) experiments arise predominantly from the use of different pre-exponential factors. Subsequently, we derive new E_{ads} values for these TPD experiments with a more accurate pre-exponential factor (while removing thermal and zero-point contributions). This effort has made it possible for this study to become the first to establish consensus between a variety of theoretical techniques and multiple experimental measurements. These estimates from both theory and experiment place the CO on MgO system squarely in the physisorption regime, all lying within the $-199 \pm 11\,\text{meV}$ range set by our best E_{ads} estimate from the cluster CCSD(T) technique. Crucially, we demonstrate that our employed cluster CCSD(T) technique, combining the recently developed SKZCAM protocol[56] with reduced-scaling CCSD(T), can achieve its high accuracy at a low cost comparable to (hybrid) DFT. This opens the door for its use as a routine benchmark tool[57–59] as well as within high-throughput frameworks for predicting new and improved catalyst[60] and gas storage materials.[61]

Methods

Before assessing the final E_{ads} obtained for the three theoretical techniques [cluster CCSD(T), periodic CCSD(T) and periodic DMC], we will discuss how we have been able to reach such high-quality estimates in this section. Each theoretical technique approaches the final E_{ads} differently based on the choice of electronic structure method [CCSD(T) or DMC] and surface model (periodic or cluster). For example, CCSD(T)[62] tackles the many-electron Schrödinger equation via an expansion of electronic configurations (using particle-hole excitation operators) from a reference wave-function while DMC[63] achieves this via an imaginary time projection to the ground state from a trial wave-function. Accordingly, these two electronic structure methods depend on different factors, such as basis set size for CCSD(T) and timestep for DMC as described in Sec. S5 of the Supporting Information. In fact, to reach sufficient accuracy, this even affects how we go about computing the E_{ads}, which we will discuss below. Thereafter, we will also describe how the the separate surface models reach the bulk limit and dilute coverage regimes.

Computing adsorption energy

The primary quantity of interest in this work is the adsorption energy, which physically represents the energy released when a CO molecule in the gas-phase adsorbs onto a pristine MgO surface and can be defined as:

$$E_{\text{ads}} = E[\text{CO+MgO}] - E[\text{MgO}] - E[\text{CO}], \tag{1}$$

where $E[\text{CO+MgO}]$, $E[\text{MgO}]$, and $E[\text{CO}]$ are the total energies of the CO on MgO (CO+MgO), gas-phase CO, and pristine MgO (001) surface systems, respectively. In practice, we actually compute the interaction energy, where we have two definitions depending on the theoretical technique:

$$E_{\text{int}} = E[\text{CO+MgO}] - E[\widetilde{\text{CO}}] - E[\widetilde{\text{MgO}}] \approx E[\text{CO+MgO}] - E[\widetilde{\text{CO}}_{\text{far}} + \widetilde{\text{MgO}}]. \tag{2}$$

The first definition is similar to E_{ads} but calculates the energy of the separate $\widetilde{\text{CO}}$ and $\widetilde{\text{MgO}}$ systems with structures frozen from the CO+MgO system (as indicated by $E[\widetilde{\text{CO}}]$ and $E[\widetilde{\text{MgO}}]$, respectively). Computing E_{int} (over E_{ads} directly) allows for basis-set superposition error (BSSE) corrections[64] to be applied for cluster CCSD(T) calculations. For periodic DMC and periodic CCSD(T), we use the second definition of E_{int}, where the $\widetilde{\text{CO}}_{\text{far}} + \widetilde{\text{MgO}}$ system corresponds to the frozen $\widetilde{\text{CO}}$ displaced >5 Å away from the frozen surface, both taken from the CO+MgO system. It differs from the (formal) first definition of E_{int} by less than 5 meV (Sec. S5.2 of the Supporting Information) and was used to mitigate finite-size errors[44] for both calculations, while also enabling larger timesteps to make DMC more economical.

Reaching the final E_{ads} from E_{int} then requires the addition of a Δ_{geom} term; it represents the energy required to relax the separate frozen CO and MgO geometries back into their equilibrium geometries. As obtaining forces (and thus equilibrium geometries) is challenging for both CCSD(T) and DMC, the CO, MgO and CO+MgO structures as well as Δ_{geom} – a small term – were approximated at the DFT level. Specifically, we chose the revPBE-D4 exchange-correlation functional[65] (and dispersion treatment[66]) due to its reasonable E_{ads} and geometrical parameters compared to CCSD(T) and experiment (see Sec. S3 of the Supporting Information). As discussed in Sec. S4 of the Supporting Information, the errors arising from the use of revPBE-D4 geometries has been conservatively estimated by assessing its effect on an ensemble of high-quality DFT functionals along Jacob's ladder.[36,67]

Periodic approaches

Assuming converged electronic structure methods (Sec. S5 of the Supporting Information), we must ensure that the surface models used (see Fig. 2) have converged to the bulk limit and dilute CO coverage regimes. Periodic approaches can achieve this in a straightforward fashion via the supercell approach (Fig. 2a) by increasing the surface supercell size and number of slab layers. As shown in Sec. S5.4 of the Supporting Information, we find that a 4 layer (4L) (4×4) supercell of the MgO (001) surface is sufficient to converge E_{ads} to less than 1 meV at the DFT level. We performed periodic CCSD(T) with the Cc4s code[51,68–70] and periodic DMC with CASINO.[71] Even with the latest advances, direct calculation (at converged settings) on the 4L (4×4) supercell is unfeasible for both periodic DMC and periodic CCSD(T). Instead, we have computed E_{int} on a 2L supercell cleaved from the original 4L supercell and, in the vein of Pople's model chemistry,[72] approximated the remaining (much) smaller contributions with computationally economical methods, as elaborated in Sec. S6 of the Supporting Information.

Cluster approaches

Cluster approaches work by placing a finite-cluster within appropriate embedding environments. They naturally provide dilute coverage estimates, but convergence towards the bulk limit is challenging. As discussed in Ref. 56, the convergence of a finite cluster depends on

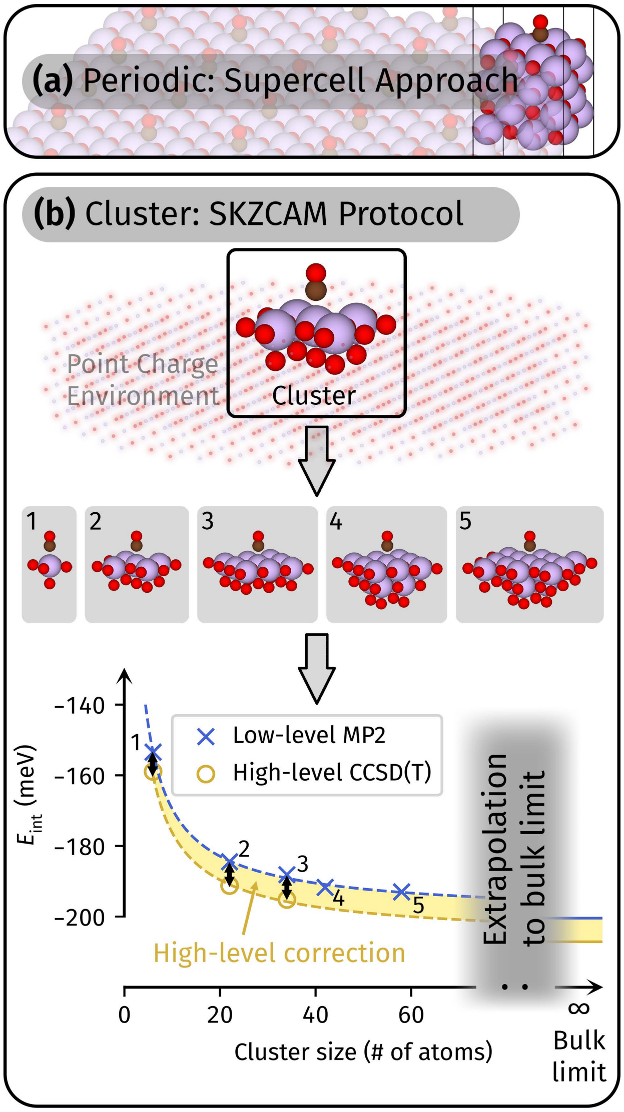

Figure 2: Schematic of the (a) periodic supercell approach and (b) cluster approach used in this study to compute the adsorption energy of CO on MgO. We perform both DMC and CCSD(T) with the periodic supercell approach. The cluster approach in (b) is based on our recently developed SKZCAM protocol,[56] which generates a series of quantum clusters of increasing size under an electrostatic embedding framework (see top panel). We have computed the interaction energy E_{int} for the first 3 (5) clusters at the LNO-CCSD(T) (MP2) level, which are numbered in the bottom panel of (b). The MP2 bulk limit was estimated by extrapolating this series of clusters. A subsequent high-level correction to the CCSD(T) level was estimated from a subset of these clusters via the LNO-CCSD(T) approach.

interdependent factors such as: (1) embedding approach (e.g., mechanical;[6] electrostatic,[73] incremental[74] or quantum[75–79]); (2) shape; (3) size; and (4) charge of the cluster. The use of steep scaling methods such as CCSD(T) severely limits the cluster size that can be reached. In this study, we use the local natural orbital (LNO) scheme[80–83] [LNO-CCSD(T)] in Mrcc[84] to further extend the feasible system sizes while maintaining high accuracy (Sec. S7 of the Supporting Information). The challenge is then to keep the (quantum) cluster small enough to make well-converged LNO-CCSD(T) computations routinely affordable, while also reaching the bulk limit.

Our recently proposed SKZCAM protocol is particularly suited for tackling this challenge. It is based upon the electrostatic embedding approach[73,85–87] (top panel of Fig. 2b) and provides the design rubrics to generate a series of quantum clusters of systematically increasing size (middle panel of Fig. 2b). We have shown previously[56] and here (bottom panel of Fig. 2b) that these clusters converge smoothly and rapidly to the bulk limit. Although initially devised for calculating oxygen vacancy formation energies, it has been extended to encompass adsorption on metal-oxide surfaces as part of this study. We take advantage of the smooth convergence with cluster size in the SKZCAM protocol to extrapolate a small number of clusters to the bulk limit. As shown in the bottom panel of Fig. 2b and Table S10 of the Supporting Information, only the first 5 clusters are required to converge to within 5 meV.

While the largest cluster size (∼60 atoms) is amenable at the MP2 level, it is intractable with canonical CCSD(T). Fortunately, convergence to the bulk limit of CCSD(T) can be accelerated by evaluating a LNO-CCSD(T) level correction to the bulk limit MP2 for a series of smaller clusters in the fashion of the ΔCC correction from Boese *et al.*[24] This correction is highly accurate because another quality of the SKZCAM protocol is the good cancellation of finite-size errors between many-body methods such as MP2 and CCSD(T) across its clusters. Specifically, we find deviations of only 3 meV in this correction across the first three clusters of the SKZCAM protocol. The resulting computations in this protocol require only a few days on a single computer node – easily accessible in commodity computer clusters.

Results

Agreement between many-body methods

As discussed in the Methods, the final E_{ads} we obtain for each of the three techniques is actually composed of several terms, where besides Δ_{geom}, E_{int} itself consists of several contributions. As shown in Sec. S6 of the Supporting Information, each of these terms have been carefully converged, with conservative error bars estimated for the most important terms. With this effort, we come to a final E_{ads} estimate (in meV) of -199 ± 11 for cluster CCSD(T), -193 ± 24 for periodic CCSD(T), and -188 ± 26 for periodic DMC (summarized in Table 1). This agreement is better than chemical accuracy, in fact, we reach sub-chemical accuracy with a maximum deviation of 11 meV (1 kJ/mol) across the three theoretical techniques, smaller than their error bars. These E_{ads} values place the adsorption behavior of CO on MgO squarely in the physisorption regime, right in the middle of the aforementioned large 500 meV range across previous theoretical calculations (Fig. 1). To give some perspective, H_2O monomers, known to chemisorb on MgO, have an E_{ads} in the -450 to -550 meV[25,42] range, close to some previous theoretical estimates for CO on MgO.

Table 1: Comparison of the final E_{ads} estimates between the cluster CCSD(T), periodic CCSD(T) and periodic DMC techniques. Estimates on the computational cost in kCPU-hours (kCPUh) and maximum RAM usage in gigabytes (GB) are also given. No RAM usage has been given for DMC because it uses a negligible amount relative to CCSD(T).

Technique	E_{ads} (meV)	Cost (kCPUh)	Max RAM (GB)
Cluster CCSD(T)	$\mathbf{-199 \pm 11}$	~20	~40
Periodic CCSD(T)	$\mathbf{-193 \pm 24}$	~200	~3000
Periodic DMC	$\mathbf{-188 \pm 26}$	~1000	N/A

Reaching agreement for the CO on MgO E_{ads} across fundamentally distinct electronic structure methods [DMC and CCSD(T)] and surface models (cluster and periodic) that have been systematically converged gives us confidence in using these estimates to evaluate past theoretical and experimental literature. In particular, the low cost of the cluster CCSD(T) approach (elaborated in the Discussion) allows for effects of electronic structure settings, such as basis set size, frozen core size and cluster size, on the E_{ads} to be studied. For example, in Sec. S8 of the Supporting Information, we show that inadequate basis set size, large frozen core size (i.e. only including valence electrons in the many-body correlation treatment) and small cluster size all lead to weaker binding (i.e. less negative E_{ads}). On the basis of this convergence analysis, we have been able to attribute many of the underestimated literature values to inadequate convergence of these properties. Similarly, we show that the studies that overestimate the binding strength largely result as they do not correct for BSSE, which becomes particularly strong for small basis sets. The advances in accuracy of the techniques in this study point towards agreement with only the work from Sauer's group, first computed by Boese *et al.*[24] then Alessio *et al.*,[25] re-affirming the reliability of their High-level:Low-level approach.[24,25,88–91]

Re-evaluating previous experimental measurements

Our reliable theoretical estimates now give us the opportunity to evaluate the discrepancies between past experiments. These previous experiments, of which there are many, have spanned a broad 300 meV range (see Sec. S2 of the Supporting Information). As discussed before[6,9,92] and in Sec. S9 of the Supporting Information, some of these measurements are not reliable and we focus only on the recent (three) temperature programmed desorption (TPD) experiments. In their original TPD measurements, (Arrhenius) activation energies (E_{act}) of -140, -192 and -155 meV were measured by Wichtendahl *et al.*,[31] Dohnálek *et al.*[32] and Sterrer *et al.*[35] respectively. Notably, there is still a deviation[24] of 52 meV ($>$1 kcal/mol) that is too large.

To compare against our theoretical calculations, the original E_{act} from TPD experiments must be converted into E_{ads}. The importance of this conversion has only been noted in a handful of recent CO on MgO studies.[10,24] Typically, it involves removing thermal and zero-point contributions, as well as pV and RT terms (i.e. effects 1, 2 and 3, but not 4, in Fig. 3a). It is common to compute these terms accurately using DFT (as performed in Sec. S9.2 of the Supporting Information). However, this only constitutes a constant shift of $-19\,\text{meV}$ for each TPD experiment, and does not solve the large noted deviation.[24] For example, with only these effects accounted for, Wichtendahl *et al.*, Dohnálek *et al.* and Sterrer *et al.* predict E_{ads} of -156, -208 and $-172\,\text{meV}$, respectively (see Sec. S2 of the Supporting Information and Fig. 1a).

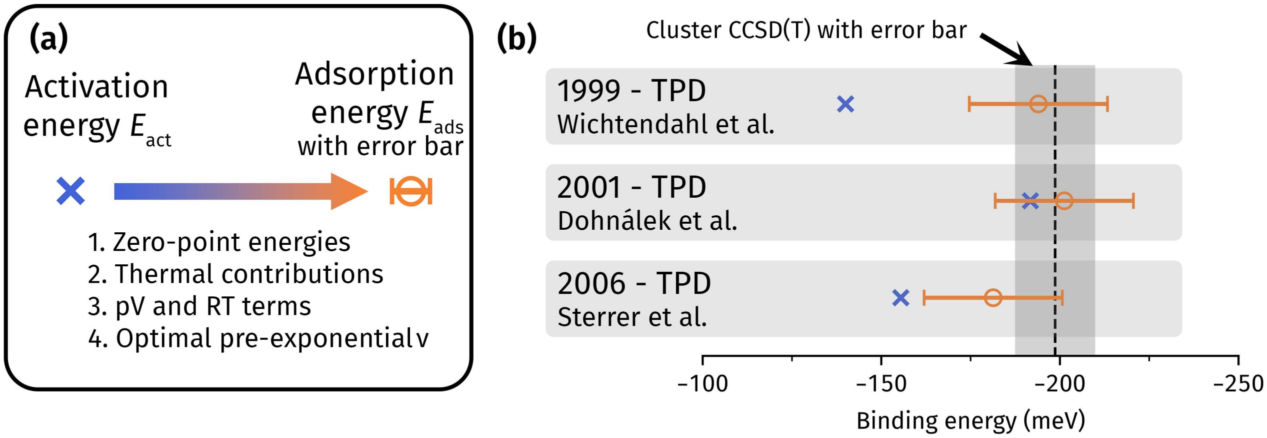

Figure 3: (a) The effects considered during conversion of the Arrhenius activation energies E_{act} in TPD experiments to adsorption energies E_{ads} suitable for comparison to theory. (b) The resulting E_{ads} converted from E_{act} match to within error bars with our cluster CCSD(T) estimate for all three TPD experiments (from Wichtendahl *et al.*,[31] Dohnálek *et al.*[32] and Sterrer *et al.*[35]).

Our theoretical estimates (between -188 and $-199\,\text{meV}$) are in the middle of the above E_{ads} range, with Wichtendahl *et al.* and Sterrer *et al.* underestimating while Dohnálek *et al.* overestimating. This differing behavior points towards the pre-exponential factor being the culprit. For example, ν is not typically known and commonly assigned to $\log(\nu) = 13$ (e.g., by Wichtendahl *et al.* and Sterrer *et al.*), while Dohnálek *et al.* have estimated (with large ± 2 error bars) it to be $\log(\nu) = 15$. Since these original experiments, ν has received considerable attention[38,93,94] and importantly, an estimate of $\log(\nu) = 13.8 \pm 1.6$ has been given by Campbell and Sellers,[95] agreeing with a theoretical estimate [$\log(\nu) = 14.2$] from

Nygren and Pettersson.[9] Thus, there is now the prospect of making corrections[38] towards a better ν value (effect 4 in Fig. 3a). In Fig. 3b, we have made these ν corrections to E_{act}, combining it with the aforementioned thermal contributions and using a newer analysis[95] of the TPD curve from the original study by Wichtendahl *et al.* The resulting experimental E_{ads} range falls to within 20 meV (i.e. sub-chemical accuracy) and all three experiments now agree with our theoretical estimates, where Wichtendahl *et al.*, Dohnálek *et al.* and Sterrer *et al.* predict E_{ads} of -194, -201 and -181 meV, respectively, with ± 19 meV error bars arising from uncertainty in ν.

Discussion

The achieved agreement is a testament to the algorithmic and methodological developments made in the past decades on all three theoretical techniques to enable such high accuracy at tractable computational cost. As discussed previously, the accuracy and reliability of the cluster CCSD(T) E_{ads} value has been made possible with the SKZCAM protocol combined with the recent advances in local approximations to CCSD(T) (e.g., LNO-CCSD(T),[80–83,96] DLPNO-CCSD(T),[97–101] PNO-LCCSD(T),[102–104] etc.). While canonical CCSD(T) could only be performed for the smallest quantum clusters of up to 1–2 dozen atoms,[83] LNO-CCSD(T) can tackle molecules involving hundreds of atoms[55,82] and ionic crystal clusters of around 100 atoms.[56] For periodic DMC, the introduction of ccECP pseudopotentials[105,106] gives confidence in calculations involving elements beyond the first row while the ZSGMA[107,108] algorithm and determinant localization approximation (DLA)[109] enable larger timesteps for the same accuracy. While DMC has had a long history spanning several decades,[42,47,110–112] the periodic CCSD(T) technique has only come into maturation in recent years[113–116] and besides the significant algorithmic improvements,[70,117] it is particularly the recent developments in finite-size corrections[51,68] which now enable chemical accuracy to be reached in solids and surfaces.[54,118,119]

We compare the computational cost of the three techniques in Table 1. While one-to-one comparison cannot be made because the calculations were performed on different computing architectures, it is clear that cluster CCSD(T) is cheaper by one or two orders of magnitude compared to either periodic techniques. In fact, this cost is comparable to periodic hybrid DFT calculations, which takes ∼1 kCPU-hours to compute, and it is expected to be even better for molecule-surface systems with larger molecules or surfaces involving heavier atoms. The cluster CCSD(T) calculations can also work on most commodity computing hardware, requiring a small amount (40 GB) of memory on one computer node, while periodic CCSD(T) can require 3000 GB of RAM distributed across several nodes. Besides its low cost, another advantage is that the accuracy and associated error bars can be kept low (by design) with the cluster calculations using the SKZCAM protocol. For example, finite-size errors from the MP2 extrapolation to the bulk limit can be estimated by including more clusters into the formula and likewise the high-level correction up to CCSD(T), as discussed in Sec. S7 of the Supporting Information. For this reason, we consider the E_{ads} estimate of $-199 \pm 11\,\text{meV}$ by the cluster CCSD(T) technique to be the most accurate out of the three. It will form the topic of future work whether the high accuracy and low cost of this cluster technique will persist for other molecule-surface systems.

The accuracy of the three theoretical techniques have come to such high precision that it is now possible to benchmark the accuracy of experiments. In particular, it has demonstrated the necessity of utilizing accurate pre-exponential factors in TPD experiments to reach reliable agreement. This means that while agreement has been achieved before for theoretical calculations and specific experiments, these must be viewed with skepticism. Out of the re-evaluated E_{ads} values in Fig. 3b, we expect the reanalyzed E_{ads} estimates from the TPD experiments by Wichtendahl *et al.* and Dohnálek *et al.* to provide a more accurate estimate than Sterrer *et al.* as they involve lower CO surface coverages (see Sec. S9.3 of the Supporting Information). As such, we take the average of the two to come to the best experimental estimate of $-198 \pm 19\,\text{meV}$ which we use in Fig. 1b. This agreement to our cluster CCSD(T) estimate of $-199 \pm 11\,\text{meV}$ is excellent, and its smaller error bars underscores its status as the best estimate to the CO on MgO E_{ads} out of all theoretical calculations and experimental measurements.

Conclusions

In summary, we have resolved the value of the adsorption energy (E_{ads}) for CO on MgO to $-199 \pm 11\,\text{meV}$, achieving consensus between three independent theoretical calculations [cluster CCSD(T), periodic CCSD(T) and periodic DMC] and three separate temperature programmed desorption experiments. It establishes both DMC and CCSD(T) as methods that have matured sufficiently to benchmark surface phenomena. For example, we used the reliable theoretical estimates to assess and understand the discrepancies in the previous literature (both theory and experiment). In particular, we demonstrate that the differences between previous experimental TPD measurements and our theoretical estimates arises from differing pre-exponential factors. A subsequent re-evaluation with more precise pre-exponential factors has now allowed for the agreement to be achieved, highlighting the importance of considering this factor in future work. Furthermore, we show that the cluster CCSD(T) technique, made possible with the SKZCAM protocol and the reduced scaling LNO-CCSD(T) technique, demonstrates high accuracy at low cost; requiring only a few days on a single computer node.

While agreement between theory and experiment has been achieved before for specific surfaces,[6,50] the SKZCAM protocol[56] used here promises the ability to generalize this accuracy to other surfaces and properties systematically, amenable for automated high-throughput calculations. Combined with its accuracy and low cost, these properties of the SKZCAM protocol opens the door towards studying the interaction of many molecules and surfaces simultaneously at reference quality with the cluster CCSD(T) technique. With this, we can create large benchmark databases suitable for assessing the quality of DFT functionals –

currently sorely lacking for metal-oxide surfaces.[93] Furthermore, we can now go beyond adsorption to study catalytic reaction steps on technologically relevant surfaces. Here, the combination of theoretical calculations and experimental measurements, now capable of reaching a consensus, will enable the unveiling of precise mechanistic insights[120,121] into these surface reaction phenomena.

Acknowledgement

The authors are grateful for: resources provided by the Cambridge Service for Data Driven Discovery (CSD3) operated by the University of Cambridge Research Computing Service (www.csd3.cam.ac.uk), provided by Dell EMC and Intel using Tier-2 funding from the Engineering and Physical Sciences Research Council (capital grant EP/P020259/1), and DiRAC funding from the Science and Technology Facilities Council (www.dirac.ac.uk); the Cirrus UK National Tier-2 HPC Service at EPCC (http://www.cirrus.ac.uk) funded by the University of Edinburgh and EPSRC (EP/P020267/1); and computational support from the UK national high performance computing service, ARCHER2, for which access was obtained via the UKCP consortium and funded by EPSRC grant ref EP/X035891/1. BXS acknowledges support from the EPSRC Doctoral Training Partnership (EP/T517847/1). VK acknowledges support from the Ernest Oppenheimer Early Career Fellowship and the Sydney Harvey Junior Research Fellowship, Churchill College, University of Cambridge. PRN is grateful for financial support from the ERC Grant No. 101076972, "aCCuracy", the János Bolyai Research Scholarship of the Hungarian Academy of Sciences, and the National Research, Development, and Innovation Office (NKFIH, Grant Nos. KKP126451 and FK142489). AM acknowledges support from the European Union under the "n-AQUA" European Research Council project (Grant No. 101071937).

Supporting Information Available

See the supplementary material for a detailed compilation of the obtained results as well as further data and analysis to support the points made throughout the text. The input and output files associated with this study and all analysis can be found on GitHub at benshi97/Data_CO_on_MgO or viewed (and analyzed) online on Colab.

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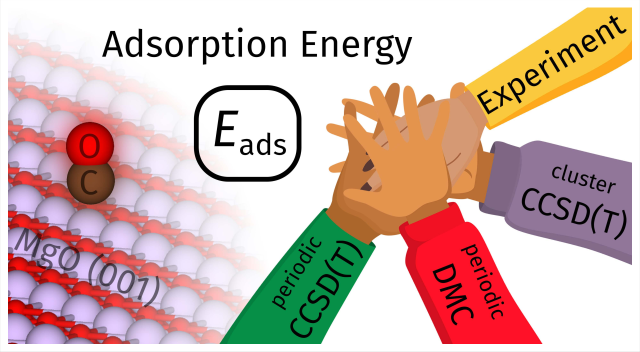
TOC Graphic


Adsorption Energy
E_{ads}
O
C
MgO (001)
Experiment
cluster CCSD(T)
periodic CCSD(T)
periodic DMC