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Approaching an exact treatment of electronic correlations at solid surfaces: The binding energy of the lowest bound state of helium adsorbed on MgO(100)

Ruth Martinez-Casado,^{1,*} Denis Usvyat,^{2,†} Lorenzo Maschio,³ Giuseppe Mallia,¹ Silvia Casassa,³
John Ellis,⁴ Martin Schütz,² and Nicholas M. Harrison^{1,5}

¹Thomas Young Centre, Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, England, United Kingdom

²Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Universitätsstrasse 31, 93040 Regensburg, Germany

³Dipartimento di Chimica, IFM, Università degli Studi di Torino, I-10125 Turin, Italy

⁴Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, England, United Kingdom

⁵Science and Technology Facilities Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England, United Kingdom

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In this work we employ *ab initio* electronic structure theory at a very high level to resolve a long standing experimental controversy; the interaction between helium and the MgO (100) surface has been studied extensively by other groups, employing diverse experimental approaches. Nevertheless, the binding energy of the lowest bound state is still unclear: the existence of a state at around -5.5 meV is well established but a state at -10 meV has also been reported. The MgO (100)-He system captures the fundamental physics involved in many adsorption problems; the weak binding is governed by long-range electronic correlation for which a fully predictive theory applicable to the solid state has been elusive. The above-mentioned experimental controversy can now be resolved on the basis of the calculations presented in this work. We performed three-dimensional vibrational dynamics calculations on a highly accurate potential-energy surface. The latter was constructed using a method which systematically approaches the exact limit in its treatment of electronic correlation. The outcome is clear: our calculations do not support the existence of a bound state around -10 meV.

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The interaction between molecules and crystalline surfaces is of great fundamental and technological interest and is extensively studied both experimentally and theoretically [1–3]. One particular example is physisorption and scattering of helium atoms on oxide surfaces. In the last two decades the latter process, employing molecular-beam techniques, has been developed into a powerful tool for the analysis of surface structure and dynamics [4–8]. It is particularly useful for studying insulating surfaces, such as MgO [4,9]. At close proximity the helium-surface interaction potential is dominated by the exponentially growing corrugated repulsive wall, which is a consequence of the mutual exchange repulsion between the helium and surface electron densities. The repulsive potential is two-dimensional (2D) corrugated and leads to a complicated diffraction pattern for helium scattered from the surface. In the range of intermediate He-surface distances, there exists a very shallow attractive potential due to the weak van der Waals interactions, which drops off with distance from the surface as $1/z^3$ [10]. Such a potential can support several bound states (in fact several 2D bands of bound states), which correspond to vibrational levels of helium atoms physisorbed on the surface.

The delicacy of the balance between different components of the helium-surface interaction makes quantitatively accurate theoretical predictions of the behavior of helium atoms on the surface extremely difficult. Standard density functional theory (DFT), which is the common tool in solid-state simulations (i.e., local-density approximation, generalized gradient approximation, or hybrids), does not capture van der Waals dispersion. In principle it can be used for calculating

the repulsive wall at the qualitative level [11–13], but for the potential well and the corresponding bound states lack of an accurate description of the dispersion interaction renders DFT too unreliable to be used as a predictive theory. An empirical *a posteriori* dispersion correction, which explicitly introduces the van der Waals-like component, can serve as a practical remedy to this problem [14], yet the crudeness and empiricism of this approach hinder quantitatively accurate first-principle predictions [15,16] (for a striking example see Fig. 5 in Ref. [16]). Even with a more rigorous MP2 description, the dispersion interaction with helium is grossly underestimated and cannot be used without higher-order correlation corrections [15,17]. A finite cluster approach facilitates, in principle, an *ab initio* treatment that can be extended to arbitrary accuracy, yet the truncation to finite cluster size results in the neglect of long-range effects and may consequently also severely compromise the accuracy at the energy scale of He-surface interaction energies.

To cope with this problem, theoretical studies of such systems usually invoke empirical reparametrization, adjusted to the experimental data [4,13,18,19]. This empirical approach cannot be used to resolve a controversy between data deduced from different experiments. Such a situation calls for an *ab initio* treatment in which the exact answer can be approached systematically. It is only very recently that such a treatment became applicable to periodic systems [20,21].

For the He-MgO(100) system there are several experimental studies in the literature reporting the energy of the ground state of adsorbed He [4,18,22,23]. In adsorption isotherm measurements of MgO smoke [23], a value of -4.8 meV for the adsorption energy was obtained. On the basis of the azimuthal angle diffraction spectra of He scattered on an *in situ* cleaved MgO(100) surface the lowest bound state was

*r.martinecasado@imperial.ac.uk

†denis.usvyat@chemie.uni-regensburg.de

found to be -5.5 meV [18]. From the spectra, obtained on an air-cleaved MgO (100) surface [4,22], however, a deeper state of -10.2 meV was measured and assigned to the ground state, while the state around -5.5 meV was assigned to the second bound state.

In order to compute a potential-energy surface for the He-MgO(100) system we employ periodic local Møller-Plesset perturbation theory of second order (periodic LMP2) [20,24,25], which is the highest-order periodic *ab initio* approach presently affordable for such a system. A reasonably large atom centered Gaussian basis set of triple-zeta quality for Mg and oxygen, and quadruple-zeta quality for He, augmented with diffuse orbitals (for oxygen and He atoms) was used (details of the basis set can be found in Ref. [15]). For further reference we denote this basis as AVTZ. The periodic LMP2 potential-energy surface (PES) was calculated as the interaction energy per helium atom between a (100) MgO three-layer slab (with an experimental lattice parameter of 4.211 Å) and a square monolayer of helium matching the surface lattice of MgO. The three-layer slab was extrapolated to the bulk limit by employing the slab replication technique [20]. Further technical details of the calculations are given in Appendix A.

It has recently been established [15,26,27] that the MP2 level of theory significantly underestimates the adsorption energy of noble gases on the MgO surface, and especially so for He. This implies that the required accuracy cannot be reached without higher-order corrections to MP2. Since such corrections are yet not possible in a purely periodic framework, we employed a finite cluster based approach as recently introduced in Ref. [27] for the study of geometrical frustration of an Ar monolayer adsorbed on MgO. According to this scheme, the intra-slab and inter-adsorbate-slab components of the LMP2 (correlation) part of the interaction energy [20,28], actually representing contributions of different physical nature [29], are scaled with appropriate factors to correct for the method and basis set deficiency of the periodic LMP2/AVTZ treatment. In contrast to other common correction schemes based on universal or empirical parameters, here the scaling factors were determined by applying a CCSD(T) (coupled cluster theory with singles, doubles, and perturbative triple excitations) treatment to a *specific finite model system featuring the same kind of interactions as the actual system of interest*. For details of the method we refer to Ref. [27] and Appendix B. For evaluating the corrections we employed the He-Mg₃Na₂O₄ dimer as the finite cluster counterpart of the periodic He-MgO system. This dimer captures the principle physics of the interaction between helium atoms and the MgO surface and, at the same time, facilitates the use of high-level quantum chemical calculations [30] and extrapolation to the complete basis set limit.

As shown in Fig. 1, the LMP2 method substantially underestimates the depth of the He-Mg₃Na₂O₄ potential. However, scaling the inter- and intramonomer LMP2 components with appropriate factors, which are given in Table I, corrects the corresponding potential curve such that it virtually coincides with the CCSD(T) one for the whole range of distances considered. The value for the intermonomer energy correction factor of 1.7 reflects the considerable underestimation of dispersion by MP2 mentioned above. At the same time, the

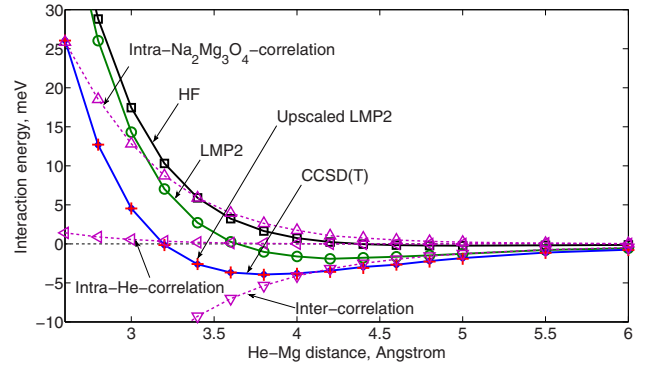


FIG. 1. (Color online) Interaction energy of the He-Mg₃Na₂O₄ dimer at the Hartree-Fock (black squares), LMP2/AVTZ (green circles), and CCSD(T)/aug-cc-pVT/QZ extrapolated (blue small filled circles) levels. The LMP2 correlation interaction energy is partitioned (magenta dashed lines) into intermolecular (down-pointing triangles), intra-Mg₃Na₂O₄ (up-pointing triangles), and intra-He components (left-pointing triangles). The LMP2 energies with the scaled intra-Mg₃Na₂O₄ (factor 1.07) and intermolecular (factor 1.71) components are denoted with red crosses.

basis set dependence of the dispersion description is rather weak, provided that diffuse functions are included in the basis sets. The intramonomer correction, on the other hand, is quite sensitive to the basis set, as expected from the locality of the Coulomb hole causing the notorious basis set convergence problem in correlated calculations.

The scaling factors were applied to the intra-MgO and inter-He-MgO components of the periodic LMP2 energies for the whole PES. Depending on the factors from Table I, the corresponding models are denoted in the following as Ups1, 2, and 3. Since the correlation contribution due to the interaction of valence electrons with the cores of Mg atoms is non-negligible [16,27], core correlation was also added. This contribution was evaluated at the periodic LMP2 level as the difference between the interaction energies obtained with the correlated *2sp* core of Mg and the frozen core approximation,

TABLE I. The scaling factors for the LMP2/AVTZ intra- and intermonomer components of the correlation contributions to the interaction energy for the Mg₃Na₂O₄-He system, obtained by fitting to the CCSD(T) potential curve, calculated with aug-cc-pVTZ (Ups1), aug-cc-pVQZ (Ups2) basis sets, and aug-cc-pVT/QZ extrapolated to the basis set limit (Ups3). The energies of the minima of the upscaled periodic LMP2 PES (including core contributions), corresponding to on-Mg and on-Mg-Mg-bridge positions, and of the laterally averaged potential, are also provided.

	Ups1	Ups2	Ups3
Scaling factors			
Intra-Mg ₃ Na ₂ O ₄	1.21	1.13	1.07
Inter-Mg ₃ Na ₂ O ₄ -He	1.67	1.69	1.71
Well depth (meV)			
On-Mg	-11.33	-11.92	-12.38
On-Mg-Mg-bridge	-9.39	-9.87	-10.24
Laterally averaged	-9.64	-10.10	-10.41

respectively [27]. For these calculations a core-consistent basis set for Mg was used (additional tight s, p, d, and f functions adopted from the cc-pwCVTZ basis [31]). Since these calculations were computationally rather demanding, the interaction of He with Mg cores was calculated only for on-Mg and on-oxygen adsorption sites, while for the rest the 2D-sine-like corrugation [27] was assumed. In fact, this component of the interaction was found to be rather uniform with respect to the adsorption position, adding about -0.8 meV at the z value corresponding to the minimum of the potential for the on-Mg adsorption site. Results for the energy minimum at on-Mg and on-Mg–Mg adsorption positions, obtained from upscaled LMP2 potentials plus core, are also given in Table I.

Once the accurate *ab initio* He–MgO PES was constructed, the energy of the vibrational ground state was calculated for the laterally averaged potential $V_0(z)$. As is evident from Table I, the well depths of the laterally averaged potentials for different models are close to the values of the corresponding original potentials at the on-Mg–Mg-bridge site, which in turn are about 2 meV higher than the values at the minima. The LMP2 and corrected LMP2 $V_0(z)$ potential curves and the energies of the corresponding vibrational ground states are displayed in Fig. 2, as well as the respective experimental estimates. The zero-point energy, i.e., the energy that has to be added to the PES minimum to yield the actual ground-state energy, ranges from $+1.5$ meV (for LMP2) to slightly more than $+2$ meV (for the corrected LMP2).

Comparison of the resulting eigenenergies with the available experimental values in Fig. 2 reveals that the MP2 bound states are indeed far too high for this system. Corrections to the CCSD(T) level and adding the core contribution substantially improves the description, placing the states in the ballpark of the experimental results: from -7.3 meV (Ups1) to -8.1 meV (Ups3). Although the calculated energies are numerically in quite good agreement with the experiment, our best theoretical

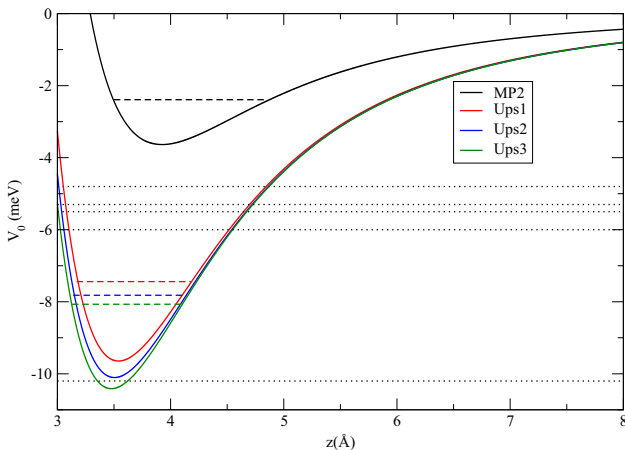


FIG. 2. (Color online) Laterally averaged potential-energy surfaces $V_0(z)$, corresponding to a progressively improved theoretical description (for details see text) and associated ground-state energies: -2.4 , -7.3 , -7.8 , and -8.1 meV. The experimental values for the lowest bound states are -4.8 [23], -5.5 [18], and -10.2 meV [4,22], and those for the second lowest state in the latter case are -6.0 [22] and -5.3 meV [4].

treatment (Ups3) positions the energy of the ground state virtually in the middle between the experimental values of Refs. [18,23] and [4,22], respectively. Hence, at that stage, no definite answer about the the existence of the -10 -meV state is possible.

Under such circumstances, it is important to estimate the sign and magnitude of the errors, remaining in the theoretical description. First, due to the smallness of the energy values considered, different technical parameters of the calculations [Hartree-Fock (HF) tolerances [32,33], fit domains [24], auxiliary basis sets [34], etc.] are responsible for a noise in the energies. However, it was found to be of the order of a few tenths of a meV in the resulting interaction energies and thus cannot substantially influence the final value. A more important issue is the possible deficiency of the model itself. There are several sources for such an error: (i) the one-dimensional (1D) approach for solving the vibrational problem, i.e., the neglect of corrugation in the potential; (ii) the basis set error in the periodic HF component of the interaction, which is not corrected in our scheme; (iii) the lack of higher than CCSD(T) correlation contributions; and (iv) the correction model employed to improve the periodic LMP2 approach, based on scaling of the intra- and intermonomer components of the interaction energy with factors obtained from finite cluster calculations. In the following we assess the importance of each of these four potential error sources.

(i) To investigate the accuracy of the 1D approximation, a full three-dimensional (3D) band-structure calculation using a plane-wave expansion of the helium wave function was performed for the Ups3 potential surface. For the details of this calculation we refer to Appendix E. The resulting 3D vibrational ground-state energy turned out to be virtually the same as that obtained by the 1D approach: -8.10 vs -8.07 meV, indicating that the 1D model indeed provides an adequate vibrational treatment for this system.

(ii) The HF basis set error does not seem to be substantial either. For the He– $\text{Na}_2\text{Mg}_3\text{O}_4$ dimer with the intermonomer distance, corresponding to the on-Mg periodic minimum (3.35 Å), the difference in the HF interaction energies between AVTZ and aug-cc-pVQZ calculations is only 0.3 meV. In the periodic calculation this discrepancy is anticipated to be even smaller, since an atomic orbital (AO) basis set in a three-layer slab is effectively larger than in a small cluster.

(iii) The effect of high-order correlation contributions beyond CCSD(T) was explored by calculating the CCSDT(Q)–CCSD(T) energy difference for a single point corresponding to the on-Mg–Mg-bridge minimum geometry (the energy at that site is very close to that of the minimum of the laterally averaged potential, *vide supra*). For these calculations the multireference coupled cluster program by Kallay [35] was employed. Since these calculations were extremely expensive, only the small He– Mg_2O_2 cluster (see Appendix C) in the cc-pVDZ(Mg)/aug-cc-pVDZ(O)/aug-cc-pVTZ(He) basis could be treated. The correction turned out to be repulsive and surprisingly large, i.e., $+1.1$ meV, indicating that our CCSD(T) well depth is noticeably overestimated, which in turn leads to a too low ground-state energy.

(iv) Finally, to check the quality of the correction protocol for improving the periodic LMP2 approach, a single point calculation at the on-Mg site geometry (minimum-energy z

position) was carried out, adopting an alternative, more rigorous, but also much more expensive correction protocol: the basis set correction was included in the periodic rather than in the finite cluster calculation by utilizing the recently implemented periodic LMP-F12 method [36]; the incremental CCSD(T)-LMP2 correction [16,37,38] was evaluated for a rather large He-Mg₉O₉ cluster in a rich basis set [cc-pVTZ(Mg)/aug-cc-pVTZ(O)/aug-cc-pVQZ(He)]; those oxygen-helium pair energies not contained in the Mg₉O₉-He cluster were upscaled in the periodic LMP2-F12 calculation by the previous factor of 1.7, i.e., according to Table I. This model yields a well depth of -10.3 meV for the on-Mg site, nearly 2 meV higher than the one predicted by the original correction protocol used for evaluating the PES.

(iii) and (iv) together shift the well depth of the potential, and with that the binding energy of the ground state, to higher energies by about 3 meV, locating it very closely to the range of -5 to -6 meV, which was assigned to the ground-state energy by some of the experiments (*vide supra*). It is unlikely that further sources of errors not considered in this work, like relativity, or the effect of even higher-order correlation contributions beyond CCSDT(Q), can yield a net stabilization of about -5 meV, which would be necessary to support a ground state at -10.2 meV. Hence, our high-quality *ab initio* treatment does not support the existence of the bound state near -10 meV. This is in accord with an alternative theoretical study, where the potential was not evaluated completely from first principles, but rather scaled to reproduce the diffraction intensities [39]. It is worth noting, that the *ab initio* potential constructed in an analogous procedure as presented here, does produce very accurate diffraction intensities [40]. Finally, we note that the theoretical potential of Ref. [19], which reproduces the ground state of -10.2 meV, was deliberately fitted to do so and thus cannot be considered as unbiased in this respect.

In experiments, uncertainties can arise from both the technological difficulties and the requirement for a correct interpretation of the spectra. First, a proper set of \mathbf{G} vectors has to be assigned to sharp peaks or sharp dips, depending on the interference (phase shift) between the direct channel and the bound-state channel [41], as sometimes different combinations of \mathbf{G} vectors can formally be valid, leading to an ambiguity in the interpretation. Moreover, it is known that the surface structure and composition can be strongly affected by preparation conditions and that great care is required if well ordered flat terraces of MgO are to be obtained [42]. The segregation of impurities to the surface and surface reconstruction have an influence on the He bound-state measurement that is difficult to quantify. Our theoretical results indicate that it might be worthwhile to revisit experimentally the He-MgO ground state.

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APPENDIX A: SPECIFICATION OF THE COMPUTATIONAL PARAMETERS

The He-MgO potential surface was calculated using a three-layer MgO slab (with an experimental lattice parameter of 4.211 Å) and a square monolayer of helium matching the surface lattice of MgO. The He-MgO PES was represented by a uniform grid consisting of 313 points. The potential curves for 21 symmetry unique adsorption sites were calculated, each sampled by 14–17 points lying in the range of 2 to 7 Å of the He-surface distance z , with the energies reaching $+20$ meV in the repulsive wall. All interaction energies were counterpoise corrected.

The HF calculations were performed using the CRYSTAL code [33]. The two-electron integral tolerances (TOLINTEG) of 7 7 7 25 75 (i.e., substantially tightened with respect to their defaults) were used. The mesh of 12×12 k points was chosen to sample the Brillouin zone. The basis set was taken from Ref. [15] (BS4). For the core correlation calculations, the tight Gaussian-type orbitals (GTOs) from the cc-pwCVTZ basis set were added for the Mg atoms.

The following orbital excitation domains [24] were chosen for the periodic LMP2 calculations: one-atom domains for the He-centered and Mg-centered (core) Wannier functions (WFs); for the oxygen atom WFs, the domains consisted of one oxygen atom and the first coordination sphere of Mg atoms (i.e., six- and seven-atom domains for the surface and bulk oxygen WFs, respectively). The WF-pair approximations were defined on the basis of the distance between the centers of the corresponding WFs. Intra-MgO-slab or intra-helium-monolayer pairs with inter-WF distance up to 6 Å were considered. Inter-slab-adsorbate pairs were included up to a distance of 12 Å. Furthermore, energy contributions from such pairs beyond 12 Å were added *a posteriori*, by assuming the C_6R^{-6} decay law and fitting the WF-pair-specific C_6 coefficients to the decay of the explicitly calculated pair energies in the range from 8 to 12 Å [20,24]. The same C_6 coefficients were used to approximate the dispersion contribution to the interaction energy from a semi-infinite MgO solid, using the slab replication technique [20]. The direct-space local robust density fitting technique [34] was employed for the two-electron integrals with interorbital distance up to 8 Å. Beyond this distance the integrals were evaluated by means of the multipolar approximation. For density fitting a combined Poisson-GTO-type fitting basis set [34,43,44] was used, which was converted [34] from the pure GTO auxiliary basis set optimized for MP2 aug-cc-pVTZ calculations [45]. The redundancy threshold for pair-domain-specific PAOs [24] was set to 10^{-5} .

APPENDIX B: THE LMP2→CCSD(T) UPSCALING CORRECTION SCHEME

This scheme was originally proposed in Ref. [27] to obtain accurate interaction energies for argon, adsorbed on MgO. It

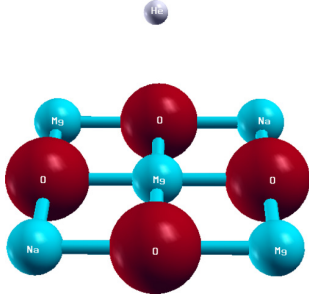


FIG. 3. (Color online) He- $\text{Na}_2\text{Mg}_3\text{O}_4$ dimer used in the LMP2 \rightarrow CCSD(T) correction scheme.

consists of upscaling the periodic LMP2 inter-adsorbate-slab and intra-MgO-slab correlation energy contributions. The corresponding correcting factors f_{inter} and $f_{\text{intra-MgO}}$ were evaluated in finite cluster calculations, carried out with the MOLPRO program [30,46]. As the prototype system, a dimer, closely related to the periodic problem under study, was taken. It consisted of a square cluster $\text{Na}_2\text{Mg}_3\text{O}_4$ with the same oxygen-metal distance as in the MgO slab and a helium atom positioned on top of the central Mg atom (Fig. 3). Two Na atoms are used to ensure the charge neutrality of the cluster, yet with the same basis as on Mg.

The counterpoise-corrected interaction energies for different He-Mg distances R_z (17 points from 2.6 to 8 Å) were calculated (i) at the CCSD(T) level with the aug-cc-pVTZ and aug-cc-pVQZ basis sets, with subsequent inverse-cubic extrapolation of the correlation energy, and (ii) with the local MP2 method in the same basis as used in the periodic calculations. Furthermore, in order to enhance the similarity between the periodic and the cluster LMP2 calculations, the computational parameters of the latter were chosen to be as close to the former as possible; i.e., (i) one-atom domains were employed for He-WFs, six-atom domains were employed for the oxygen WFs, and each oxygen atom was surrounded by additional ghost Mg atoms; and (ii) the same localization procedure (Boys [47]) and PAO redundancy threshold (10^{-5}) were used as in the periodic case.

The correlation part of the LMP2 *interaction* energy was partitioned [28] into intra- $\text{Na}_2\text{Mg}_3\text{O}_4$ energy $\Delta E_{\text{intra-MgO}}^{\text{LMP2}}$, intrahelium energy $\Delta E_{\text{intra-He}}^{\text{LMP2}}$, and intermonomer $\Delta E_{\text{inter}}^{\text{LMP2}}$ energy components. The scaling factors $f_{\text{intra-MgO}}$ and f_{inter} were obtained by minimizing

$$\sum_{R_z} (\Delta E^{\text{CCSD(T)}} - \Delta E_{\text{intra-He}}^{\text{LMP2}} - f_{\text{intra-MgO}} \Delta E_{\text{intra-MgO}}^{\text{LMP2}} - f_{\text{inter}} \Delta E_{\text{inter}}^{\text{LMP2}})^2. \quad (\text{B1})$$

APPENDIX C: CCSDT(Q)-CCSD(T) CORRECTION

This correction was calculated as the CCSDT(Q)-CCSD(T) energy difference for a He- Mg_2O_2 cluster (Fig. 4). The Mg-O distance in the square Mg_2O_2 cluster was taken the same as in the MgO crystal. The helium atom was placed atop the bridging Mg-Mg point with a separation of $R_z = 3.5$ Å from the latter. This distance corresponds to the minimum of the periodic potential surface for the bridging adsorption site, calculated within the Ups3 model. The MRCC code

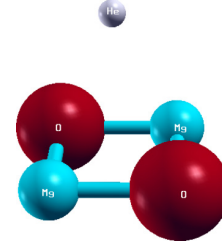


FIG. 4. (Color online) He- Mg_2O_2 dimer used for the CCSDT(Q)-CCSD(T) single point energy correction.

of Kallay [35], interfaced with the MOLPRO program, was used. Since the CCSDT(Q) method is very expensive, the CCSDT(Q)-CCSD(T) energy difference was calculated at the cc-pVDZ(Mg)/aug-cc-pVDZ(O)/aug-cc-pVTZ(He) [48] basis set level only.

APPENDIX D: INCREMENTAL CCSD(T) CORRECTION TO THE PERIODIC LMP2-F12 INTERACTION ENERGY

In order to estimate the magnitude and the sign of the error of the energy upscaling model (see above), we performed an alternative evaluation of the interaction energy between the MgO surface and the helium atom placed at the global minimum of the potential surface. It corresponds to the on-Mg adsorption site and a distance of $R_z = 3.35$ Å. To minimize possible errors of the periodic HF/LMP2 calculations, a five-layer slab and a large fitting basis set were taken. The latter corresponded to Weigend's basis, optimized for MP2 calculations with a quintuple-zeta AO basis set [45], and converted to a combined Gaussian/Poisson basis set according to the procedure of Ref. [34]. The $2sp$ core electrons of Mg were also correlated.

The basis set error correction was evaluated also in the periodic framework, employing the recently implemented periodic LMP2-F12 method [36] in the 3*A fixed-amplitude approximation [49–51]. The periodic F12 correction was evaluated using a three-layer MgO slab. For the density fitting and resolution of the identity approximation the same extended auxiliary basis set was used as for the LMP2 calculations.

The periodic LMP2-F12 interaction energy was further corrected by adding the frozen-core CCSD(T)-LMP2 energy difference, calculated on a He- Mg_9O_9 cluster (Fig. 5) with the cc-pVTZ(Mg)/aug-cc-pVTZ(O)/aug-cc-pVQZ(He) [48] basis set. To correct the complete dispersion energy to the CCSD(T) level, the periodic frozen-core LMP2 energies of the inter-MgO-He pairs, which do not appear in the He- Mg_9O_9 cluster, were upscaled with the factor 1.7. This factor represents the LMP2 method error correction for the inter-MgO-He energy (see Table I) and is virtually independent from the basis set quality (*vide supra*).

The interaction energy components, calculated in this way, have the following values: (1) periodic HF, +4.71 meV; (2) frozen-core periodic LMP2 (with the upscaled inter-He-MgO energies), -10.08 meV; (3) the periodic F12 correction, -0.76 meV; (4) the core contribution, -0.81 meV; and (5) the CCSD(T)-MP2 energy difference in the He- Mg_9O_9 cluster, -3.33 meV. This in total yields -10.27 meV.

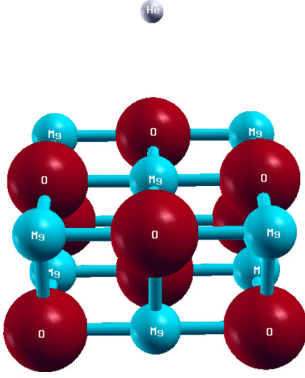


FIG. 5. (Color online) He-Mg₉O₉ dimer used for the CCSD(T)-MP2 single point energy correction.

APPENDIX E: CALCULATION OF THE VIBRATIONAL LEVELS, USING THE 3D HELIUM-MGO POTENTIAL SURFACE

Due to the 2D periodicity of the surface, the bound states of helium on MgO form 2D Bloch waves, and a rigorous calculation of their energies would require a 2D-periodic+1D-non-periodic approach. However, in case of shallow corrugation a simplified 1D model is commonly employed for such calculations [3,4,18,19]. To this end, from the 2D Fourier expansion of the PES $V(\mathbf{r})$ [$\mathbf{r} = (x, y, z) = (\mathbf{R}, z)$],

$$V(\mathbf{R}, z) = V_0(z) + \sum_{\mathbf{G} \neq 0} V_{\mathbf{G}}(z) e^{i\mathbf{G} \cdot \mathbf{R}}, \quad (\text{E1})$$

where \mathbf{G} labels the surface reciprocal-lattice vectors; only the zeroth-order term, i.e., the laterally averaged potential $V_0(z)$, is adopted to calculate the bound states.

TABLE II. The parameters for the Buckingham pairwise potential, fitted to the Ups3 potential-energy surface, where $A_{\text{He}X}$ and $C_{\text{He}X}$ are, respectively, the repulsive and attractive coefficients of the He- X interactions (where $X=\text{O}$ and Mg).

X	$A_{\text{He}X}$ (meV Å ^{m})	$\rho_{\text{He}X}$ (Å)	$C_{\text{He}X}$ (meV Å ^{6})
O	2.4×10^5	3.3×10^{-1}	11.9×10^3
Mg	4.5×10^{-1}	4.8×10^{-1}	2.0×10^{-1}

We tested both approaches. First the bound states were calculated by solving the 1D anharmonic vibrational Schrödinger equation with the $V_0(z)$ potential, using the Numerov algorithm [52]. In order to check the accuracy of the 1D model, the energies of the Γ -point vibrational states of the real 3D potential surface were also evaluated.

The latter was represented by the Buckingham model potential [39], fitted to the Ups3-scaled LMP2 potential surface, using the gulp program [53]. The fitted parameters are given in Table II.

The energy of the lowest vibrational state within the full 3D potential-energy surface was calculated in a plane-wave basis. The natural x and y periodicity, corresponding to the 2D periodicity of the surface, was accompanied by a model z periodicity (with a very large period), created by imposing the periodic boundary conditions in this direction. The 2D band structure of vibrational and translational states for the He-MgO Ups3 potential was evaluated. The bottom of the lowest band (occurring actually at the Γ point) yields the energy of the lowest bound state, which within the Ups3 potential was found to be -8.29 meV. For a closer link to the experimental value, we also introduced the approximation of uncoupled xy and z modes, which is usually implied within the analysis of the spectra. For the energy of the incident beam of 18.8 meV, used in Ref. [4], the corresponding correction turned out to be very small: $+0.19$ meV, leading to the final result of -8.10 meV for the energy of the lowest vibrational state within the 3D Ups3 potential.

- [1] S. Miret-Artés, *Surf. Sci.* **339**, 205 (1995).
- [2] S. Miret-Artés, J. P. Toennies, and G. Witte, *Phys. Rev. B* **54**, 5881 (1996).
- [3] A. Sanz and S. Miret-Artés, *Phys. Rep.* **451**, 37 (2006).
- [4] G. Benedek, G. Brusdeylins, V. Senz, J. G. Skofronick, J. P. Toennies, F. Traeger, and R. Vollmer, *Phys. Rev. B* **64**, 125421 (2001).
- [5] J. R. B. Gomes and J. P. P. Ramalho, *Phys. Rev. B* **71**, 235421 (2005).
- [6] D. Farias and K.-H. Rieder, *Rep. Prog. Phys.* **61**, 1575 (1998).
- [7] R. Guantes, A. Sanz, J. Margalef-Roig, and S. Miret-Artés, *Surf. Sci. Rep.* **53**, 199 (2004).
- [8] F. Tuddenham, H. Hedgeland, J. Knowling, A. Jardine, D. MacLaren, G. Alexandrowicz, and J. E. W. Allison, *J. Phys.: Condens. Matter* **21**, 264004 (2009).
- [9] K. H. Rieder, *Surf. Sci.* **118**, 57 (1982).
- [10] G. Vidali, G. Ihm, H.-Y. Kim, and M. W. Cole, *Surf. Sci. Rep.* **12**, 135 (1991).
- [11] R. Martinez-Casado, B. Meyer, S. Miret-Artés, F. Traeger, and C. Woell, *J. Phys.: Condens. Matter* **19**, 305006 (2007).
- [12] R. Martinez-Casado, B. Meyer, S. Miret-Artés, F. Traeger, and C. Woell, *J. Phys.: Condens. Matter* **22**, 304011 (2010).
- [13] A. Schüller, D. Blauth, J. Seifeert, M. Busch, H. Winter, K. Gärtner, R. Włodarczyk, J. Sauer, and M. Sierka, *Surf. Sci.* **606**, 161 (2012).
- [14] S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).
- [15] R. Martinez-Casado, G. Mallia, D. Usvyat, L. Maschio, S. Casassa, M. Schütz, and N. M. Harrison, *J. Chem. Phys.* **134**, 014706 (2011).
- [16] S. Tosoni and J. Sauer, *Phys. Chem. Chem. Phys.* **12**, 14330 (2010).
- [17] A. Heßelmann, *J. Chem. Phys.* **128**, 144112 (2008).

- [18] M. Mahgerefteh, D. R. Jung, and D. R. Frankl, *Phys. Rev. B* **39**, 3900 (1989).
- [19] B. Johnson and R. J. Hinde, *J. Phys. Chem. A* **115**, 7112 (2011).
- [20] C. Pisani, M. Schütz, S. Casassa, D. Usvyat, L. Maschio, M. Lorenz, and A. Erba, *Phys. Chem. Chem. Phys.* **14**, 7615 (2012).
- [21] G. Booth, A. Grüneis, G. Kresse, and A. Alavi, *Nature (London)* **493**, 365 (2012).
- [22] G. Brusdeylins, R. B. Doak, J. G. Skofronick, and J. P. Toennies, *Surf. Sci.* **128**, 191 (1983).
- [23] T. S. Sullivan, A. D. Migone, and O. E. Vilches, *Surf. Sci.* **162**, 461 (1985).
- [24] C. Pisani, L. Maschio, S. Casassa, M. Halo, M. Schütz, and D. Usvyat, *J. Comput. Chem.* **29**, 2113 (2008).
- [25] D. Usvyat, B. Civalleri, L. Maschio, R. Dovesi, C. Pisani, and M. Schütz, *J. Chem. Phys.* **134**, 214105 (2011).
- [26] R. Martínez-Casado, G. Mallia, and N. M. Harrison, *Chem. Commun.* **47**, 4385 (2011).
- [27] D. Usvyat, K. Sadeghian, L. Maschio, and M. Schütz, *Phys. Rev. B* **86**, 045412 (2012).
- [28] M. Schütz, G. Rauhut, and H.-J. Werner, *J. Phys. Chem. A* **102**, 5997 (1998).
- [29] J. Langlet, J. Caillet, J. Bergès, and P. Reinhardt, *J. Chem. Phys.* **118**, 6157 (2003).
- [30] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, *Comput. Mol. Sci.* **2**, 242 (2011).
- [31] K. A. Peterson and T. H. Dunning, *J. Chem. Phys.* **117**, 10548 (2002).
- [32] C. Pisani, R. Dovesi, and C. Roetti, *Hartree-Fock Ab Initio Treatment of Crystalline Solids*, Lecture Notes in Chemistry Series Vol. 48 (Springer-Verlag, Berlin, 1988).
- [33] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush *et al.*, *CRYSTAL09 User's Manual* (Università di Torino, Torino, 2010).
- [34] M. Schütz, D. Usvyat, M. Lorenz, C. Pisani, L. Maschio, S. Casassa, and M. Halo, in *Accurate Condensed Phase Quantum Chemistry*, edited by F. R. Manby (CRC, Boca Raton, FL, 2010), p. 29.
- [35] M. Kallay and J. Gauss, *J. Chem. Phys.* **123**, 214105 (2005).
- [36] D. Usvyat, *J. Chem. Phys.* **139**, 194101 (2013).
- [37] A. D. Boese and J. Sauer, *Phys. Chem. Chem. Phys.* **15**, 16481 (2013).
- [38] C. Müller and D. Usvyat, *J. Chem. Theory Comput.* **9**, 5590 (2013).
- [39] R. Martínez-Casado, G. Mallia, D. Usvyat, L. Maschio, S. Casassa, M. Schütz, and N. M. Harrison, *Phys. Chem. Chem. Phys.* **13**, 14750 (2011).
- [40] R. Martínez-Casado, D. Usvyat, G. Mallia, L. Maschio, S. Casassa, M. Schütz, and N. M. Harrison, *Phys. Chem. Chem. Phys.* (2014), doi:10.1039/c4cp01145g.
- [41] G. Benedek, P. M. Echenique, J. P. Toennies, and F. Traeger, *J. Phys.: Condens. Matter* **22**, 359801 (2010).
- [42] O. Robach, G. Renaud, and A. Barbier, *Surf. Sci.* **401**, 227 (1998).
- [43] F. R. Manby, P. J. Knowles, and A. W. Lloyd, *J. Chem. Phys.* **115**, 9144 (2001).
- [44] J. W. Mintmire and B. I. Dunlap, *Phys. Rev. A* **25**, 88 (1982).
- [45] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- [46] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, *Molpro, Version 2010.1, A Package of Ab Initio Programs* (2011), <http://www.molpro.net>
- [47] S. F. Boys, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P. O. Löwdin (Academic, New York, 1966), pp. 253–262.
- [48] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- [49] S. Ten-no, *Chem. Phys. Lett.* **398**, 56 (2004).
- [50] H.-J. Werner, T. B. Adler, and F. R. Manby, *J. Chem. Phys.* **126**, 164102 (2007).
- [51] R. A. Bachorz, F. A. Bischoff, A. Glöß, C. Hättig, S. Höfener, W. Klopper, and D. P. Tew, *J. Comput. Chem.* **32**, 2492 (2011).
- [52] J. W. Cooley, *Math. Comput.* **15**, 363 (1961).
- [53] <https://projects.ivec.org/gulp/>