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Ab initio study of the symmetric reaction path of H_2 with a surface V center in magnesium oxide

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An all-electron *ab initio* calculation, including correlation effects, of the symmetric reaction path of H_2 with a surface V center in magnesium oxide has been carried out. The importance of lattice relaxation effects has been demonstrated, and the position of the saddle point has been located. The calculated barrier to the reaction, 40 kcal mol^{-1}, is considerably greater than the value necessary for H_2-D_2 exchange at 78 K, suggesting that the lowest-energy pathway involves the asymmetric interaction of H_2 with the surface V center.

I. INTRODUCTION

The use of *ab initio* methods to study the energetics and reaction pathways of simple chemical reactions is now well established.[1] In particular, the explicit inclusion of electron correlation has been shown to be essential in the estimation of activation barriers involved in bond rupture and formation.[2] For systems consisting of up to four or five first-row atoms, calculations close to the Hartree-Fock limit, followed by configuration-interaction (CI) and/or multiconfiguration self-consistent-field (MCSCF) expansions, can yield results comparable in accuracy to experiment, with energy differences of 2–3 kcal mol^{-1}.[2] At this level of accuracy, studies to date have been primarily concerned with *in vacuo* reactions.[1–3] However, there exists a large body of surface-catalyzed reactions, of both fundamental and practical importance, that require theoretical understanding.[4] Many of these involve insulators, including a wide range of oxides,[5] and are thought to occur at point and extended surface defects.[6] Now the treatment of such imperfections requires careful consideration, for there is substantial evidence that indicates that in materials such as oxides, elastic relaxation, in the bulk and at the surface, plays a critical role in determining both the energy and atomic configuration associated with lattice defects.[7] Recent developments in the atomic simulation of ionic materials enable the calculation of this relaxation, the importance of which has been noted in materials ranging from MgO to sodium–β-alumina.[8]

In this paper we show that *ab initio* quantum-chemical methods at the accuracy referred to earlier, and hence suitable for reaction-path investigation, can be combined with defect-lattice simulation procedures to yield a realistic description of the dissociative chemisorption of hydrogen at a V center in the $\{100\}$ surface of MgO. Less extensive calculations along similar lines have recently been reported for the dissociative interaction of a hydrogen molecule with a self-trapped hole (O^-) and V^- center at this same lowest-index surface.[9]

II. EXPERIMENTAL BACKGROUND

Reactions such as the ortho-para conversion of hydrogen and the hydrogen-deuterium exchange reaction,

$$H_2+D_2\rightleftharpoons 2HD\ ,$$

are known to be catalyzed by the transition metals, W, Ni, and Pt,[10] by the transition-metal oxides Cr_2O_3, NiO, and Co_3O_4,[11] and also by MgO under certain circumstances.[12] The activity of the transition metals and their oxides is attributed to the presence of d orbitals at or near the Fermi level that overlap the ${}^1\Sigma_g^+$ ground state of hydrogen. MgO, on the other hand, has no such low-lying d orbitals, and it has been shown that catalytic activity is not due to any transition-metal impurities.[13] However, it is known that γ- and uv-irradiated MgO is catalytically active at 78 K *after irradiation;* this has been attributed to paramagnetic O^- centers in the surface, particularly in the form of V and V^- centers.[13–17] In some cases residual OH^- groups associated with the cation vacancy have been found.[14,16] The formal mechanism for the reaction can be considered as

$$\{O_O^- - V_{\mathrm{Mg}} - O_O^-\}_{\mathrm{surface}} + H_2(g) \rightleftharpoons \{(OH)_O^- - V_{\mathrm{Mg}} - (OH)_O^-\}_{\mathrm{surface}} \cdot$$

There is also speculation and some experimental evidence[18,19] that {111} microfaces of MgO comprising three O^- ions in a triangular array dissociatively chemisorb hydrogen. It is thought that the active center here involves a self-trapped proton, although the detailed geometric structure is not clear.

III. THEORETICAL CONSIDERATIONS

In the study reported here our model for the dissociative chemisorption of hydrogen involves the symmetric interaction of molecular H_2 with a V center at the {100} surface of MgO. To investigate the potential energy surface for this reaction we must consider the following:

(i) the local lattice configuration of the V center,
(ii) the electronic structure of the lattice in the vicinity of this defect, and
(iii) the accurate treatment of the incoming H_2 molecule interacting with the two O^- ions of the defect.

We now consider each of these theoretical aspects in turn.

A. Defect-lattice simulation

The theory of defect-lattice simulation has been described in detail recently[20]; for completeness we summarize the salient features. Our treatment is derived from that developed by Lidiard and Norgett[21,22] and applied to the surface-defect structure of MgO and other fcc materials.[7,23] It involves application of the Mott-Littleton approximation[24] to the lattice statics formulation of Kanzaki.[25] The lattice surrounding a defect is arbitrarily partitioned into two regions, an inner region immediately surrounding the defect and an outer region, which is normally at least three lattice separations away from the defect. The essence of the simulation is to minimize the *force* on each ion surrounding the defect. This is accomplished by an explicit relaxation of the ions in the inner region, while the displacement in the outer region is calculated on the basis of the Mott-Littleton approximation. It is a matter of experience[26] that approximately 100 ions need to be explicitly relaxed for convergence of the local force and total defect energy. In the present calculations we have considered an inner region of 97 ions consisting of a $7 \times 7 \times 2$ surface array at the V center.

In the defect-lattice simulation, as opposed to the reaction-path calculation, two-body potentials are assumed, with an explicit allowance for electronic polarization by means of the shell model of Dick and Overhauser.[27] Here, as elsewhere,[23] we have used a modified form of the electron-gas approximation[28–30] to evaluate ionic two-body interactions. The use and application of this approximation in defect-lattice simulations have been discussed in detail previously.[31] In general, electron-gas potentials lead to *zero-strain* bulk lattices approximately 3—5 % larger than experiment: For MgO the corresponding lattice parameters are 2.171 and 2.106 Å, respectively. However, this expansion seems to have very little effect on either defect energies or lattice configurations. Our calculations show that the nondefective {100} surface of MgO dilates and rumples very little from the perfect-lattice structure (2% and 0.7%, respectively). The relaxed defective surface, on the other hand, is appreciably distorted. The two O^- ions of the V center are displaced by 0.273 Å from their perfect-lattice positions, the two surface O^{2-} ions by 0.359 Å, and the O^{2-} below the Mg vacancy by 0.162 Å. The relaxation of the next-nearest-neighbor Mg^{2+} and more distant ions is markedly less, as might be expected. The relaxed configuration at the surface V center is shown in Fig. 1. Since the V center is overall neutral in charge, the outer region contribution to the total energy and local defect structure is small, of the order of 0.2%. For this reason the subsequent electronic structure calculations have included the effects of the 97 inner region ions only.

B. Electronic structure of MgO

MgO is a wide-band-gap (7.8 eV) insulator that is generally thought to be appreciably ionic, though this is a matter of some speculation. The electronic structure has been described on a number of occasions, notably by Kunz and co-workers.[32,33] Calculations introducing periodic lattices need no assumptions as to the degree of ionicity, for this emerges from the self-consistent description of the electronic structure. On the other hand, calculations of the type discussed here involve *nonperiodic* lattices, which are most conveniently described in terms of finite clusters of ions embedded in point-ion fields, and it is the use of such fields that necessitates assumptions as to the ionicity of the lattice. Recent calculations[34] involving MgO, $(MgO)_2$, and $(MgO)_4$ clusters in self-consistent point-ion fields, however, have indicated that lattice MgO, as opposed to diatomic MgO, is almost totally ionic with absolute effective charges in excess of 1.99*e*. Accordingly, calculations reported here are based on point-ion fields with charges of $\pm 2e$. The basis sets employed were various contractions[35] of Huzinaga's (9*s*5*p*) basis[36] for oxygen and Veillard's (12*s*6*p*) basis[37] for magnesium. Close agreement was found between the calculated O^--O^{2-} energy separation for a (4*s*2*p*) contraction and that derived using the uncontracted oxygen basis. This double-zeta oxygen basis was used in conjunction with various contractions of the Mg (12*s*6*p*) basis to study the effect of the lattice on the electronic structure of MgO. It is worth noting that while the essential ionicity of lattice MgO is insensitive to the details of the basis set used for the cluster, the charge distribution for free or diatomic MgO seems to be much more dependent on the magnesium basis employed. A minimal basis set optimized for Mg^{2+} predicts (free) MgO to be ionic, whereas the use of larger basis sets leads to a high degree of covalency as shown in Table I.

In our model of the surface *V* center we consider explicitly the five nearest-neighbor oxygen ions; that is to say, four ions (two O^{2-} and two O^-) in the surface plane and a single O^{2-} ion directly beneath the vacancy. Thus we treat the *V* center as a 48-electron system. Point charges of ± 2 were placed at the remaining relaxed lattice sites of region 1. Our system, therefore, is overall neutral.

Electronic structure calculations at varying levels of sophistication were carried out on the above-mentioned 48-electron system, which has effective C_{2v} symmetry. A double-zeta basis, constructed from the uncontracted functions previously described, was employed. The three O^{2-} ions form an effective closed-shell system, while the ten valence 2*p* electrons on the two O^- ions are to be distributed among six valence molecular orbitals (MO's) constructed from the 2*p* orbitals on these two centers. A SCF calculation of the lowest triplet spin state led to the following configuration for these ten valence electrons:

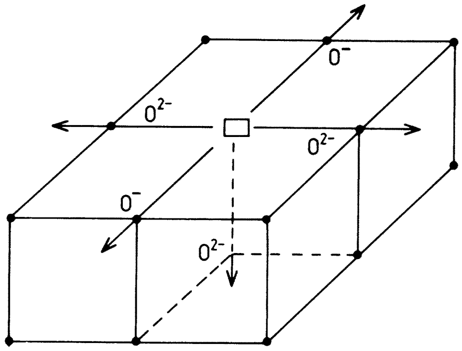

FIG. 1. Nearest-neighbor relaxation around the Mg^{2+} surface *V* center shown by arrows that are the atomic displacement (×3).

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 2b_2^1 2a_1^1 , \tag{1}$$

where the $1a_2$ and $1b_1$ orbitals are constructed from the atomic p_y functions and the $1b_2$,$1a_1$ and $2b_2$,$2a_1$ orbitals from atomic p_x and p_z functions, respectively. With the $1b_2$ and $1a_1$ MO's dominated by p_x and the $2b_2$ and $2a_1$ MO's by p_z, each O^- ion has the effective atomic configuration $2p_x^2 2p_y^2 2p_z^1$. We have also carried out restricted Hartree-Fock (RHF) calculations on the corresponding closed-shell singlet configurations arising from double occupancy of the nearly degenerate $2b_2$ and $2a_1$ orbitals:

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 2b_2^2 , \tag{2}$$

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 2a_1^2 , \tag{3}$$

which were found to be nearly degenerate ($\Delta E = 0.00168$ hartree) and to both lie nearly 0.3 hartree above the $^3B_2$ state (1). The near-degeneracy of the two $^1A_1$ states suggests that for a realistic description of the $^1A_1$ state a two-configuration SCF treatment is needed. This was accomplished by use

TABLE I. Total SCF energies (hartree) and atomic charges (Q_{Mg},Q_O) in gaseous and solid MgO as a function of the Mg basis set.

	Gaseous			Solid		
Contraction	E_{SCF}	Q_{Mg}	Q_O	E_{SCF}	Q_{Mg}	Q_O
Uncontracted[a]	−274.3192	0.6	−0.6	−300.7917	2.0	−2.0
(6*s*2*p*)[b]	−274.3016	0.6	−0.6	−300.7647	2.0	−2.0
(3*s*1*p*)[b]	−274.2936	0.6	−0.6	−300.7641	2.0	−2.0
(2*s*1*p*)[b]	−274.0401	2.0	−2.0	−300.7572	2.0	−2.0

[a] Mg, 12*s*6*p*; O, 9*s*5*p*.
[b] (9*s*5*p*|4*s*2*p*) on O.

of the antisymmetrized product of strongly orthogonal geminals (APSG) method[38] in which the $2b_2$ and $2a_1$ orbitals are assigned to a geminal describing the singlet coupling of the unpaired density on the two O^- ions. This led to the two-term ${}^1A_1$ state being nearly degenerate $[E({}^3B_2)-E({}^1A_1)=0.002$ hartree] with the ${}^3B_2$ state, a not unexpected result in view of the large separation of the two O^- ions (4.88 Å).

A more accurate treatment of the relative disposition of the ${}^3B_2$ and ${}^1A_1$ surface states was obtained through multireference single-excitation configuration-interaction (MRS-CI) calculations. In the MRS-CI calculations, the configuration space consists of a number of reference configurations together with those generated by single excitations from these reference configurations. Such a procedure is designed to provide a balanced treatment of the whole potential energy surface by correcting any inadequacies in the basis APSG natural orbitals, although of course, recovering only a limited amount of correlation energy. These calculations were carried out by the method to be described for the H_2 + surface-*V*-center system, with the H_2 molecule removed far from the surface. The small splitting between the ${}^1A_1$ and ${}^3B_2$ state $[E({}^3B_2)-E({}^1A_1)$ $=-0.001$ hartree] again illustrates the near-degeneracy of these two states. In contrast to APSG and RHF treatments, the MRS-CI study predicts the ${}^3B_2$ state to lie lower in energy than the ${}^1A_1$ state. Although this is in agreement with experiment where the defect is found to be paramagnetic in nature, the result may be fortuitous in view of the somewhat restricted basis and level of CI invoked.

C. Interaction of H_2 with a surface *V* center

Our investigation of the dissociative chemisorption of hydrogen described here is based on the symmetric approach of H_2 to a $\{100\}$ surface *V* center in MgO, which is similar to that used by Derouane *et al.*[39,40] The potential energy surface associated with the reaction

$$\{O_O^- - V_{\mathrm{Mg}} - O_O^-\}_{\mathrm{surface}} + H_2(g)$$
$$\rightleftharpoons \{(OH)_O^- - V_{\mathrm{Mg}} - (OH)_O^-\}_{\mathrm{surface}}$$

can be described in terms of two coordinates, the H—H bond length (r) and the vertical distance of the H_2 molecule from the surface (R). Thus we study the approach of a H_2 molecule along the C_{2v} reaction path, using the fixed coordinates of the relaxed lattice as previously described. We now describe the accurate calculation of the electronic wave functions for the 50-electron system consisting of three O^{2-} ions, two O^- ions, and the H_2 molecule. The electrons involved in the chemical reaction are the ten p electrons on the O^- ions and the two H_2 electrons. When the H_2 molecule is far from the surface (large R) and close to its equilibrium bond length, the symmetric ${}^1A_1$ ground state of the total system is described by the coupling of $H_2({}^1\Sigma_g^+)$ with the ${}^1A_1$ state of the *V* center, in terms of the two configurations

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 2b_2^2 2a_1^2 \tag{4}$$

and

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 2a_1^2 3a_1^2 \;, \tag{5}$$

where the $2a_1$ MO correlates with the $1\sigma_g$ orbital of H_2 and the $3a_1$ orbital with the O^- p_z orbitals. For longer r, a further ${}^1A_1$ configuration

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 (2b_2 2a_1)(3a_1 3b_2) \tag{6}$$

(where parentheses denote singlet coupling of the enclosed orbitals) will become important. Here the $2a_1$ and $3b_2$ orbitals correlate with the σ_g and σ_u orbitals of H_2, respectively. This configuration permits dissociation to the ${}^3B_2$ state of the lattice and $H_2({}^3\Sigma_u^+)$.

For small R and r near its equilibrium value, configurations (4) and (5) will again dominate the wave function. An increase in r will result in the formation of two O—H bonds neighboring the lattice vacancy. In this region of the energy surface the single configuration

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 2b_2^2 2a_1^2 \tag{6'}$$

with the $2b_2$ and $2a_1$ orbitals now predominantly O—H bonding in character is a satisfactory description. However, a correct description of H—H bond cleavage in this region of the energy surface requires two additional configurations, namely,

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 2b_2^2 3b_2^2 \tag{7}$$

and

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 3a_1^2 3b_2^2 \;, \tag{8}$$

where $3b_2$ correlates with the $1\sigma_u$ orbital of H_2. Thus, a MCSCF calculation involving configurations (4)—(8) would provide optimal orbitals for use in a subsequent CI expansion. However, a two-pair APSG representation of the wave function in which the orbitals involved in each pair are $(2b_2,3a_1)$ and $(2a_1,3b_2)$ includes configurations (4), (5), (7), and (8) and provides a more economic way of obtaining suitable MO's than a general MCSCF calculation. The APSG method was used to obtain orbitals suitable for performing the subsequent CI calculations. In the latter the $1s$ and $2s$ oxygen orbitals were frozen and the high-energy core-complement orbitals omitted when generating the configuration space, resulting in 39 active MO's and 30 active electrons. Preliminary MRS-CI calculations using configurations (4)—(8) as references, together with the configuration

$$1a_2^2 1b_1^2 1b_2^2 1a_1^2 (2b_2 3b_2)(2a_1 3a_1) \qquad (9)$$

[configurations (6) and (9) forming a two-membered canonical set], suggested that four additional configurations were important. The final MRS-CI calculations were carried out using this ten-term reference set, resulting in a configuration space of 1587 bonded functions.[41] All calculations were carried out on the Cray-1S computer of the Science and Engineering Research Council Daresbury Laboratory.

IV. DISCUSSION

A. Calculated potential energy surface

In Table II we show the calculated energy of the V-center—H_2 system relative to that of the $^3B_2$ state of the defect and two ^2S hydrogen atoms for a representative set of points on the potential energy surface. At each distance of the H_2 molecule above the surface (R) an energy minimum is found close to the equilibrium bond length for free H_2 (0.746 Å). For large R, the depth of this well is merely the calculated dissociation energy of H_2, 91 kcal mol^{-1}, compared to the experimental value of 104.2 kcal mol^{-1}.[42] The depth of this well decreases as the molecule approaches the surface, yielding a barrier of 22 kcal mol^{-1} for the insertion of H_2 into the surface. For H-H separations close to r_e, the dominant configurations in the CI expansion are (4) and (5), corresponding to the interaction of $H_2(^1\Sigma_g^+)$ with the $^1A_1$ state of the V center. For values of R less than 4.0 Å, a second energy minimum occurs at larger values of r, when the dominant configuration (6') corresponds to the formation of two O—H bonds. The depth of this second potential well increases as R decreases, corresponding to the approach of the O-H separation to its equilibrium value in OH^- (0.94 Å). There is a distinct barrier between these two minima that leads to an activation energy barrier for the reaction. In this region of the energy surface the CI wave function contains significant contributions from all the configurations (4)—(7). The global energy minimum occurs at $R=0.8$ Å and $r=3.4$ Å and corresponds to an O—H bond length of 1.0 Å. At this position the hydrogen atoms are neither in the surface nor sited directly above the O^- species. The potential energy surface for the reaction is shown in Fig. 2, which, together with the data of Table II, shows that the saddle point for the reaction occurs close to $R=0.5$ Å and $r=1.4$ Å with an energy barrier of 40 kcal mol^{-1}. This represents a significant reduction from the calculated dissociation energy of free H_2 (91 kcal mol^{-1}), thus illustrating the potentially catalytic nature of this particular surface defect.

B. Comparison with previous calculations

A number of additional calculations were carried out to examine certain aspects of the model used in this study. In particular, we have initially considered the following.

(a) The incorporation of a diffuse p function ($\zeta=0.059$) on the O^- ion of the V center. These functions have been found to be important in providing an adequate description of certain molecular anionic species.[43]

(b) The explicit inclusion of two Mg^{2+} ions as next-nearest neighbors to the cation vacancy of the V center.

(c) The effects of omitting lattice relaxation.

Each of these factors was analyzed by means of APSG calculations at two limits of the potential energy surface, namely, where the H_2 molecule is far removed from the surface and where OH^- groups have actually formed in the surface. A H—H bond length of 0.746 Å was taken for H_2 distant from the

TABLE II. MRS-CI energies for the surface reaction H_2 + defect MgO. All energies are given in units of kcal mol^{-1} relative to the energy of the $^3B_2$ defect and two H ^2S atoms.

R (Å) \ r (Å)	0.6	0.746	1.0	1.4	2.0	3.0	4.0	4.877	5.6
4.0	−74.8	−91.1	−78.8	−42.6	−10.4	0.4	0.2	0.0	0.0
2.0	−74.1	−90.1	−77.3	−40.5	−11.3	−20.0	−28.3	−31.7	−22.9
1.635	−73.3	−89.1	−76.0	−39.3	−20.3	−45.4	−73.3	−88.4	−78.0
1.5	−72.8	−88.6	−75.4	−38.9	−26.3	−59.7	−97.1	−115.6	−101.8
1.0	−70.4	−86.0	−72.2	−41.4	−62.6	−154.2	−207.8	−188.9	−176.7
0.5	−66.3	−80.4	−66.8	−50.5	−108.4	−203.4			
0.0	−59.1	−69.1	−57.1	−48.8	−119.8	−186.5			

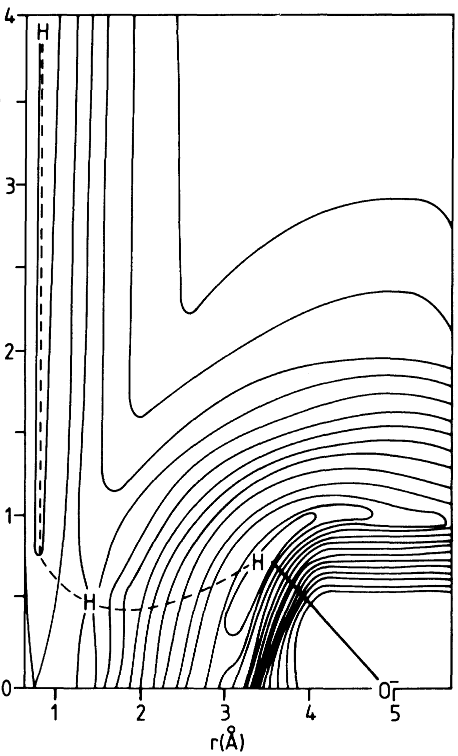

FIG. 2. Potential energy surface for the reaction $H_2 + 2O^- \rightarrow 2OH^-$ occurring at a surface *V* center in MgO; --- represents the minimum-energy pathway. Contours are drawn at intervals of 0.025 hartree.

surface and an O—H bond length of 0.94 Å (taken from the minimum-energy point of the MRS-CI study) used at the other extreme point. In the calculation that omitted lattice relaxation, an O^--O^- distance of 4.34 Å was used, to be compared with a separation of 4.88 Å in the relaxed lattice. The results given in Table III show that both the additional *p* function and explicit inclusion of the two Mg^{2+} ions have little effect on the relative energetics and formal charge distributions. However, the neglect of lattice relaxation leads to nearly twice the energy separation, in addition to quite large effects on the calculated atomic charges. An important effect of the lattice relaxation, therefore, is to remove the spatial equivalence of the four surface oxygen ions and thus localize the spin density at two centers.

Finally, the energetics of the saddle point for the reaction were investigated as a function of both basis set and degree of electron correlation invoked. A (10*s*6*p*) basis on oxygen and a (5*s*) set for hydrogen was contracted (5*s*3*p*|3*s*),[44] with polarization functions added to the O^- centers ($\zeta_d = 1.28$) and hydrogen atoms ($\zeta_p = 0.75$),[45] leading to a basis of 92 functions. We included all single and double excitations from those configurations exhibiting a CI coefficient greater than 0.075 in the final CI wave functions. This resulted in a four-reference, 79 878 secular problem at the asymptote (H_2 at a large distance from the surface) and a seven-reference, 229 939 secular problem at the saddle point, with all virtual orbitals retained in the excitation space. A computed barrier of 39 kcal mol^{-1} is given by these calculations, in excellent agreement with the value of 40 kcal mol^{-1} derived from the more modest treatment used to describe the entire surface. These results also demonstrate the minor roles played by the polarization functions on the barrier height, analogous CI calculations omitting these functions from the basis leading to a barrier of 37 kcal mol^{-1}.

Previous calculations of this symmetric pathway have been limited to single determinantal supermolecule treatments. Thus, Derouane *et al.*[39,40] have carried out minimal—basis-set SCF calculations for

$$[\text{Mg—O—H}\ \ V_{\text{Mg}}\ \ \text{H—O—Mg}]^{2+}$$

in a study of the symmetric dissociation of H_2 to form two OH^- ions at a notional vacancy. These authors obtained a barrier height of 4 kcal mol^{-1}, which is significantly less than the value of 22 kcal mol^{-1} found in our CI treatment (see Table II). We have further investigated the single determinantal approximation by computing the SCF potential

TABLE III. Results of APSG calculations on alternative models. I denotes H_2 distant from the defect; II denotes two OH^- in the surface.

	Assumed model		Mg^{2+} in surface			Diffuse *p* on O^-		Unrelaxed lattice	
				Energy (hartree)					
I	−449.4866		−846.7534			−449.5428		−448.8838	
II	−449.5842		−846.8577			−449.6472		−449.0805	
I−II	0.0976		0.1043			0.1044		0.1967	
				Atomic charges					
	O	H	Mg	O	H	O	H	O	H
I	−1.0	0.0	2.0	−1.0	0.0	−1.1	0.0	−1.7	0.0
II	−1.3	0.3	2.0	−1.3	0.3	−1.5	0.3	−1.6	0.5

curves for H_2 in the surface ($R=0$) using both a minimal Slater-type orbital (STO-3G) (Ref. 46) and double-zeta basis described previously. We find no barrier to the formation of OH^- suggesting that the barrier found by Derouane *et al.* arises from an inadequate treatment of the lattice. Kunz and Guse[33] studied the chemisorption of H atoms on a neutral molecular cluster $(MgO)_3$ to simulate the $\{111\}$ microface of three O^- ions that has been alleged to exist.[18] They conclude that virtually zero activation energy is required for the chemisorption of up to two hydrogen atoms into their model surface. This agrees with previous calculations[9] and with our present findings (see Table II and Fig. 1) from which it is clear that separated H atoms will readily bond to the surface by reacting with the two O^- ions of the surface *V* center.

V. CONCLUSIONS

The calculations reported here are the most detailed to date for the dissociative chemisorption of hydrogen at an oxide surface. They have demonstrated the importance of both lattice relaxation and correlation effects in a proper description of a surface reaction and have indicated the ways in which these may be included in a "supermolecule" treatment of the reaction. By comparison with "state of the art" calculations at the asymptote and saddle point, we have demonstrated that a modest CI treatment is sufficiently accurate to describe the energetics of the saddle point. With regard to the theoretical techniques used, an improved treatment would include a further optimization of the lattice configuration as a function of the hydrogen positions. The principal deficiency of the present calculations is that they have concentrated solely on the *symmetric* interaction of H_2 with the surface *V* center. Our calculated barrier of 40 kcal mol^{-1}, while substantially less than the computed dissociation energy of hydrogen (91 kcal mol^{-1}), is appreciably greater than the actual value, which must be close to zero for ortho-para conversion and H_2-D_2 exchange at 78 K, although this has not been determined accurately. We conclude, therefore, that the lowest-energy pathway for the dissociative chemisorption of hydrogen involves the *asymmetric* interaction of hydrogen with the surface *V* center. This is supported by previous, less exact calculations of the interaction of H_2 with a self-trapped hole (O^-) at the $\{100\}$ surface of MgO.[9] Mapping the complete energy hypersurface, including the lowest-energy path, at the level described here involves much more extensive calculations, which we intend to consider in the future.

In summary then, the present calculations, despite the deficiencies noted above, have identified two important theoretical features that would seem to be necessary for the determination of reaction paths at surfaces. We have shown that accurate quantum-chemical treatments, which include lattice relaxation, can yield useful information about potential catalytic processes.

ACKNOWLEDGMENT

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