

Quantum Mechanical Approach to the Chemisorption of Molecular Hydrogen on Defect Magnesium Oxide Surfaces

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Quantum mechanical theoretical calculations have been performed on the linear atomic chain $(\text{MgOHV}_{\text{Mg}}\text{HOMg})^{2+}$ in order to simulate the interaction of molecular hydrogen with the defects present at the surface of activated MgO. The total energy of the system, the relative energy of the various molecular orbitals, and the electronic charge distribution have been computed for various lattice parameters ($d_{\text{O-O}} = 4.0\text{--}4.8 \text{ \AA}$) as a function of the H-H (or O-H) separation. A symmetrical motion of the hydrogen nuclei with respect to the central Mg^{2+} vacancy was assumed. It is shown that chemisorption of hydrogen on surface O^- ions sites results in the formation of pseudo-hydroxyl groups. For a small lattice parameter (4.0 Å), no stable state of molecular hydrogen has been found while an increase in the lattice parameter results in a uniform increase of the calculated activation energy for the molecular hydrogen activation process. A mechanism is proposed which is not so different from that put forward for the hydrogen activation by transition metal complexes. Molecular hydrogen is found to act as an electron donor.

Key words: Chemisorption of H_2 to defect Mg oxide surfaces – Hydrogen, chemisorption of, to defect Mg oxide surfaces

1. Introduction

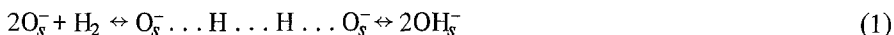
Few chemical reactions occur at 78°K. This is because of the long lifetime of activated or so-called unstable intermediates at such a low temperature. It is therefore remarkable that the $\text{H}_2\text{--D}_2$ isotopic exchange is occurring on several solid catalysts, even at the temperature of liquid nitrogen.

Such catalysts can be metals as W, Ni, or Pt [1] or transition metal oxides as NiO , Cr_2O_3 , and Co_3O_4 [2]. The ability of these for activating and dissociating the hydrogen molecule is related to the presence of the metal atom or ion d -orbitals, in analogy with the hydride ligand formation by soluble complexes of various transition metals [3].

During the last five years, a decent amount of work has been devoted to the investigation of the activation of molecular hydrogen by non-transition metal oxides, and in particular

by MgO [4–8]. Boudart *et al.* [4] have shown that MgO powder, suitably activated under 10^{-5} torr at 500°C , was able to catalyze the $\text{H}_2\text{-D}_2$ equilibration at 78°K , with no need for irradiation, with a turnover number comparable to that currently observed in enzyme or homogeneous catalysis. The activity was attributed to the presence of a very particular site, consisting of a paramagnetic center, V_T , a triangular array of O^- ions, and a nearby residual hydroxyl group. Other paramagnetic sites were also identified [5] in which protons from hydroxyl groups were completely exchangeable by molecular H_2 at room temperature or below.

More recent work, based on electric conductivity [6] or ESR measurements [7] on activated MgO samples, under hydrogen pressure, also indicated that molecular hydrogen activation was occurring and resulting, in this particular case, in the formation of pseudo-hydroxyl groups according to the mechanism:



s, referring to surface species.

In a recent paper [8] we made theoretical computations for this reaction (1) by considering, as a model, the linear atomic chain $(\text{MgOHV}_{\text{Mg}}\ddot{\text{H}}\text{OMg})^{2+}$, where V_{Mg} stands for an Mg^{2+} ion vacancy. We found evidence for the existence of a stable state of molecular hydrogen in interaction with the pseudo-surface, i.e., $(\text{MgOV}_{\text{Mg}}\ddot{\text{H}}\text{OMg}, \text{H}_2)^{2+}$, for the possibility of a thermal dehydration mechanism resulting in the formation and desorption of molecular hydrogen (which was already observed by mass spectroscopic measurements [9]), and we proved that molecular H_2 activation on such electron defect sites was expected to occur with a very small activation energy (about $4 \text{ kcal} \cdot \text{mol}^{-1}$).

Obviously, there are no available *d*-orbitals. Hence, another mechanism must be proposed. The purpose of this paper is to present a detailed picture of the OH bond formation, following H_2 activation, or dissociation, with H_2 release, namely by a careful orbital population analysis, by varying the lattice parameter (the O–O separation), and by making a quantitative comparison between our theoretical results and the available experimental data. As before [8], molecular hydrogen is supposed to interact with a pair of O^- ions imbedded in the MgO lattice. We think that this approach is likely to throw some light on the activation mechanism of molecular hydrogen by non-transition metal oxide surfaces.

2. Experimental

2.1. The Model Surface

Various reasons led us to choose the model shown in Fig. 1. It consists of a linear atomic chain with a total charge of +2, indicating that the oxygen ions are formally in the oxidation state -1 . V_{Mg} stands for a vacancy of Mg^{2+} (using Kröger's symbols [10]). a_0 is the lattice parameter equal to the O–O distance or to twice the Mg–O distance, R being the O–H separation.

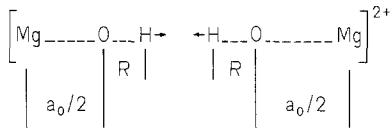


Fig. 1. Linear atomic model used to simulate the interaction of molecular hydrogen with the MgO surface

We find in this model the cationic vacancy in the neighborhood of which H₂ release has been postulated to occur [9], and the electronic defect centers O⁻ which are responsible for the hydrogen activation.

The relatively small size of this model, although 40 electrons are to be considered, renders possible detailed and exhaustive calculations.

2.2. The Theoretical Method

Ab initio calculations have been performed in the framework of the standard single determinantal molecular orbital (MO) theory.

The polyelectronic wave function is approached by an anti-symmetrized product of mono-electronic molecular orbitals doubly occupied by electrons with antiparallel spins. The molecular orbitals are described using the LCAO approximation in which each orbital is developed in terms of the various atomic functions centered on the different nuclei of the molecule. The atomic functions are atomic Slater orbitals (1s for H, 1s, 2s, 2p_x, 2p_y, and 2p_z for O, 1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, and 3p_z for Mg) which are approached by least-square fitting to a sum of three Gaussian functions.

The computations have been performed using the Gaussian 70 program of Hehre and Pople [11] on an IBM 370/168 computer.

3. Results and Discussion

3.1. Validity of our Approach

We have used the same approach in a previous work [8] to evaluate the possibility of molecular hydrogen release from thermally activated hydrated MgO surfaces. The model and the method which we used allowed us to explain most of the experimental features, giving us some confidence in our approach in spite of the relative simplicity of our model surface.

Better tests are to be found which are more directly related to the energy of the molecular orbitals describing the system and to the description of the chemical bonds which are involved.

A first test would be to compare the computed MO energy values to those measured experimentally by X-ray photoelectron spectroscopy.

Table 1 shows the energy variation of the successive MO's when the O-H distance, R , is varied, the lattice parameter, a_0 , being equal to 4.2 Å, i.e. the value for bulk MgO. When $R = 0.980$ Å, which corresponds to the position of the total energy minimum assigned to the system (2Mg²⁺, 2OH⁻) (see Sect. 3.2), one has a set of energy levels which

Table 1. Energy of the successive molecular orbitals as a function of R ^a

Orbital ^b	Type	$R = 0.500$	$R = 0.750$	$R = 0.936c$	$R = 0.980d$	$R = 1.300$	$R = 1.500$	$R = 1.698e$
Mg(1s)	K	-49.0801	-49.0700	-49.0691	-49.0692	-49.0671	-49.0514	-49.0264
O(1s)	K	-20.2740	-20.1786	-20.1684	-20.1710	-20.2080	-20.2800	-20.3935
Mg(2s)	L _{2s}	-4.1550	-4.1472	-4.1471	-4.1474	-4.1467	-4.1343	-4.1143
Mg(2p _x , 2p _y)	L _{2p}	-2.5953	-2.5873	-2.5871	-2.5873	-2.5885	-2.5709	-2.5482
Mg(2p _z)	L _{2p}	-2.5905	-2.5828	-2.5830	-2.5833	-2.5823	-2.5688	-2.5476
OH(2σ ² , with O(1s), 2s)	1σ _g	-1.4883	-1.3703	-1.2698	-1.2579	-1.2235	-	-
and H(1s))	1σ _u	-1.4880	-1.3697	-1.2682	-1.2562	-1.2202	-	-
O(2s)	1σ _g	-	-	-	-	-	-1.2585	-1.3250
O(2s)	1σ _u	-	-	-	-	-	-1.2547	-1.3223
MgOH(3σ ² , with Mg(3s,	2σ _g	-0.7081	-0.6776	-0.6430	-0.6366	-0.6093	-	-
3p _z), O(2s, 2p _z), H(1s)	2σ _u	-0.7069	-0.6734	-0.6272	-0.6168	-0.5198	-	-
OH(H(1s) and O(2p _z))	2σ _p	-	-	-	-	-	-0.6552	-0.7810
OH(H(1s) and O(2p _x))	2σ _u	-	-	-	-	-	-0.4458	-0.4054
O(2p _x , 2p _y)	1π _{g,u}	-0.4991	-0.4560	-0.4341	-0.4331	-0.4480	-0.5005	-0.5814

^a $a_0 = 4.2$ Å (equilibrium distance in bulk MgO); R values in Å; energy in atomic units, 1 a.u. = 27.204 eV or 2.1947×10^5 cm⁻¹ or 6.2771×10^2 kcal.

^b Major contribution in terms of LCAO coefficients of atomic orbitals.

^c Equilibrium O-H distance in hydroxides [12].

^d Equilibrium O-H distance (optimized geometry) for this model.

^e Equilibrium H-H distance (optimized geometry, $d(\text{H-H}) = 4.2 - 2R$) for this model.

is comparable, in principle, to the one experimentally observed for $\text{Mg}(\text{OH})_2$. This view is supported, in addition, by the fact that the optimized value of R which we compute, 0.980 Å, is very close to the equilibrium O-H distance measured in the hydroxides [12].

The various molecular orbitals are identified by the major contribution in terms of the LCAO coefficients of the atomic orbitals or by their symmetry. Core levels are denoted in the usual manner by K ($1s$ levels) and L ($2s$ and $2p$ levels).

Table 2 compares the computed values to the experimental values as given by ESCA [13]. The ESCA shifts have been incremented by the work function of gold ($\phi_{\text{Au}} = 4.9$ eV), the latter being used as reference. As the theoretical values are computed in the

Table 2. Experimental and theoretical energy of the successive molecular orbitals^a

Orbital	Calculated Value	Corrected Value ^b	Experimental Values	
			$\text{Mg}(\text{OH})_2^c$	Free OH ^{-d}
$\text{O}(2p_x, 2p_y); 1\pi_{g,u}$	-11.78	-9.69	-9.70	-2.905
$\text{MgOH}; 2\sigma_u$	-16.68	-13.81	-13.70	-6.902
$\text{MgOH}; 2\sigma_g$	-17.32	-14.25	-14.30	-
$\text{OH}; 1\sigma_{u,g}$	-34.17	-28.12	-28.00	-24.631
$\text{Mg}; L2p_z$	-70.28	-57.84	-53.60	-
$\text{Mg}; L2p_x, 2p_y$	-70.38	-57.92	-53.60	-
$\text{Mg}; L2s$	-112.83	-92.86	-92.50	-
$\text{O}; K$	-548.73	-	-534.00	-548.894
$\text{Mg}; K$	-1334.88	-	-	-

^a $a_0 = 4.2$ Å, $R = 0.980$ Å (optimized geometry for the O-H distance in our model); all energy values in eV.

^b Calculated value corrected for accounting of the Koopmans approximation [16], the correction factor has been determined by least-square fitting to be of 0.823.

^c ESCA binding energies incremented of the work function of Au ($\phi_{\text{Au}} = 4.9$ eV); values from Ref. [13].

^d See Refs. [14] and [15].

approximation of Koopmans' theorem [16], which neglects electronic relaxation associated with ionization, corrected values have to be calculated by multiplying the theoretical values by a constant factor smaller than unity. A least-square fit correlation between the theoretical and experimental data shows it to be equal to 0.823 in the present case. After correction, excellent agreement is observed between the calculated and measured values, which gives us increased confidence in our approach.

In addition, the theoretical results enable the unambiguous assignment of all the lines observed in the ESCA spectrum and comparison with the free hydroxyl group data [14, 15] shows that the hydroxyl group in the hydroxide is very similar to the free hydroxyl, but for the fact that all levels are shifted to lower energies by about 4 eV as a result of the positive potential due to the Mg^{2+} cations.

Another test is to compare the calculated electronic distribution in the system to the experimental one as derived, for example, from the ionicity of the Mg-O bond.

In the Pauling scale, Mg has an electronegativity of 1.2 compared to 3.5 for O [17]. Hence, it can be shown that for such a difference in electronegativity the single Mg-O bond must have about 74% ionic character.

Fig. 2 shows the variation of the atomic electronic populations on Mg, O, and H when R is varied ($a_0 = 4.2 \text{ \AA}$). When $R = 0.980 \text{ \AA}$, a distance at which we have hydroxyl groups, the Mg-O bond is almost a single bond. The calculated electronic charge on Mg is $10.527e^-$, which indicates that it is a $\text{Mg}^{+1.473}$ ion. This value is in astonishing agreement with the predicted Pauling value $\text{Mg}^{+1.48}$, as 100% ionicity corresponds to Mg^{2+} .

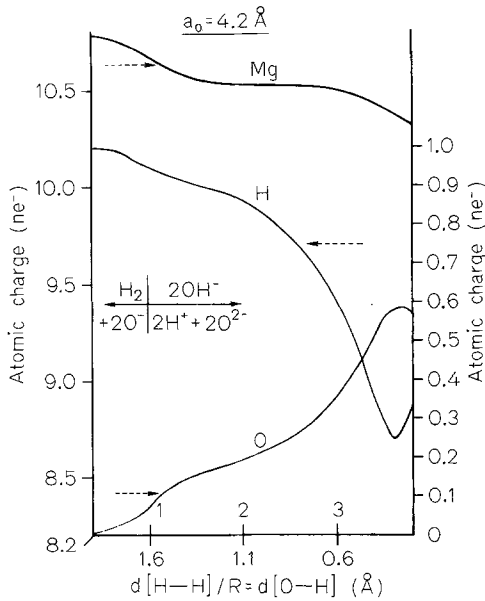


Fig. 2. Variation of the atomic electronic populations on Mg, O, and H in the system $(\text{MgOHV}_{\text{Mg}}\text{HOMg})^{2+}$ as a function of R ($a_0 = 4.2 \text{ \AA}$)

Finally, the computed total energy curves (or energy potentials) can be parametrized to fit the expected anharmonic potential as given by second-order perturbation theory. We have recently shown [18] that this enabled the calculation of the successive vibration energy levels for both chemisorbed H_2 and hydroxyl groups, in excellent agreement with experimental infrared spectroscopy data.

The former results hence indicate that our approach provides a satisfactory description of the interaction of H_2 with defects at the surface of MgO .

3.2. Effect of the Lattice Parameter on the Interaction of H_2 with the Surface of a Face-Centered Cubic Oxide

Boudart *et al.* [4] have shown, in their study of the H_2 - D_2 isotopic exchange at 78°K , the major influence of the energetic (activation energy) and geometric parameters. At 78°K , MgO shows an activity 700 times higher than NiO and 100.000 times greater than CaO . These three oxides are face-centered cubic and it is not impossible that these

differences in activity arise from the variation in the lattice parameter (although a contribution of *d*-orbitals is also possible for NiO). Indeed, a_0 (MgO) = 4.2 Å as compared to a_0 (CaO) = 4.8 Å and a_0 (NiO) = 4.1 Å.

With the theoretical computations for the systems $(\text{CaHOV}_{\text{Ca}}\text{HOCa})^{2+}$ and $(\text{NiOHV}_{\text{Ni}}\text{HONi})^{2+}$ being more difficult than for the Mg case, because of the much higher number of orbitals to be considered, we chose to consider the same model $(\text{MgOHV}_{\text{Mg}}\text{HOMg})^{2+}$ (see Fig. 1) in which a_0 is now varied between 4.0 and 4.8 Å.

Obviously this is an oversimplification, hence our results have only to be considered as a first approximation to the description of the CaO and NiO systems. They are probably more relevant for CaO than for NiO, as we cannot reject in the latter the more or less important role played by the *d*-orbitals.

We have calculated, for several values of a_0 (4.0, 4.2, 4.4, 4.6, and 4.8 Å), the total energy of the system and the electronic population in the different atomic orbitals variations as a function of R .

Fig. 3 shows the effect of a_0 on the shape of the total energy curves as a function of the H-H distance ($d_{\text{H-H}} = a_0 - 2R$). The highest energy minimum, near 0.7–0.8 Å, corresponds to chemisorbed H_2 while the lowest energy minimum is assigned to the formation of hydroxyl groups [8].

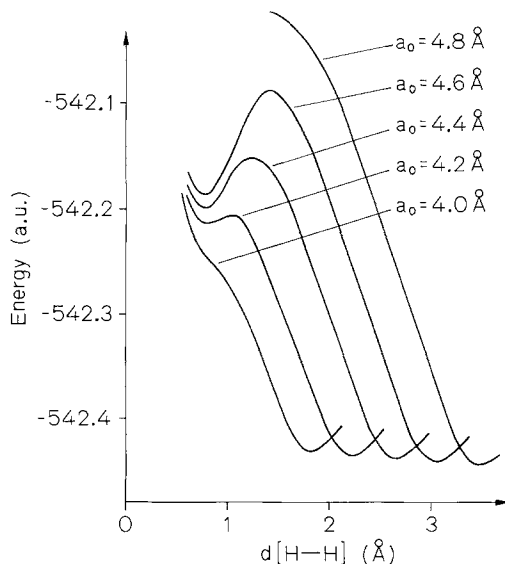


Fig. 3. *Ab initio* potential functions for the system $(\text{MgOHV}_{\text{Mg}}^i\text{HOMg})^{2+}$ for various values of a_0

Increasing $d_{\text{H-H}}$ values correspond to the reactive chemisorption of hydrogen, resulting in the formation of hydroxyl groups. The following conclusions immediately result from these data:

- a) the optimized equilibrium H-H distance decreases with increasing a_0 values, tending towards 0.74 Å, which is the internuclear distance in the free molecular hydrogen;

- b) the energetic barrier separating both minima increases rapidly with a_0 ;
 c) the energy difference between both minima also increases with increasing a_0 ;
 d) finally, there is no stable state for chemisorbed H_2 (no apparent minimum) when $a_0 = 4.0 \text{ \AA}$.

These data enable the discussion of the reactive chemisorption of hydrogen, or of its eventual release, according to Eq. (1), as a function of the value of a_0 .

Table 3 summarizes the computed activation energy values for the latter reactions.

Table 3. Lattice parameter effect on the activation energies for the processes:



and



a_0 (Å)	$E_a^{(1)}$ (kcal · mol ⁻¹)	$E_a^{(2)}$ (kcal · mol ⁻¹)	Remarks
4.0	-	-	No stable state of chemisorbed H_2
4.2	145.0	4.1	-
4.4	181.6	29.1	-
4.6	221.5	63.6	-
4.8	-	-	Very high activation energies. No hydrogen activation or release

When $a_0 = 4.0 \text{ \AA}$ there is no stable state for molecular H_2 chemisorbed on an O^- ion pair. Hence, H_2 will react irreversibly leading to the formation of hydroxyl groups.

For $a_0 = 4.2 \text{ \AA}$ (which is the case of MgO), there is a stable state for chemisorbed H_2 which can react with a very small activation energy to form hydroxyls. The reverse process is characterized by a much larger activation energy. It is, however, not impossible.

The activation energies associated to the chemisorption and release of hydrogen processes increase rapidly with a_0 in the range 4.2–4.8 Å. Hence, the probability of both processes will progressively decrease. When $a_0 = 4.8 \text{ \AA}$ the energy barrier is almost equal to the dissociation energy of hydrogen. Hence no hydrogen activation results.

Another interpretation of these data is possible by presenting them in terms of dissociation energies, which is done in Table 4. Indeed, the total energy curves can be considered as the sum of three potentials corresponding respectively to two hydroxyl groups and one hydrogen molecule [8].

The computed dissociation energy values are always smaller than the corresponding values for the isolated molecules, the effect being much larger for the hydrogen than for the hydroxyl group dissociation. Hence, one concludes that the dissociation energy

Table 4. Dissociation energies of H₂ and OH⁻ as a function of a₀

a ₀ (Å)	D _e (OH ⁻) (kcal · mol ⁻¹)	D _e (H ₂) (kcal · mol ⁻¹)
4.0	-	0.0
4.2	72.5	4.1
4.4	90.8	29.1
4.6	101.7	63.6
OH ⁻ (gas phase)	102.4	-
H ₂ (gas phase)	-	104.2

of molecular hydrogen is decreased by interaction with the active surface; this is obviously a “catalytic” effect when this process is reversible.

Hence, these data seem to indicate that the important decrease in catalytic activity which is observed when going from MgO to CaO is probably and essentially due to a geometric effect, an increase in the lattice parameter resulting in a rapid increase of the activation energy. The lower, although not negligible, activity of NiO can eventually be attributed to the poorly defined state of chemisorbed molecular H₂ when a₀ is smaller than 4.2 Å.

The first indication on the mechanism by which H₂ is activated is obtained by considering the variation in the atomic orbital populations as a function of *R* and a₀. Fig. 4 shows the electronic populations in the different orbitals of H, O, and Mg as a function of a₀, respectively, at the H-H equilibrium (dashed line) and O-H equilibrium (plain line) distances, as obtained from the total energy curves shown in Fig. 3.

It is found that the electronic population observed at the O-H minima are almost independent of the value of a₀. The two minima which correspond to chemisorbed molecular hydrogen, as observed for a₀ = 4.2 and 4.4 Å, essentially differ by the electronic population in the O(2p_z) orbital. It is of 0.370 when a₀ = 4.2 Å as compared to 0.296 when a₀ = 4.4 Å.

The reactive chemisorption of hydrogen has a major effect on the electronic population of the Mg(3s), O(2p_z), and H(1s) orbitals, which are all valence MO's. When going from the chemisorbed H₂ configuration to the di-hydroxyl system, the following changes are observed when a₀ = 4.2 Å (see also Fig. 2), H(1s): -0.16e⁻, O(2p_z): +0.66e⁻, Mg(3s): -0.35e⁻, and O(2s) = -0.22e⁻. This results in a weakening of the H-H bond, the formation of new O-H bonds, and a small decrease in the ionic character of the Mg-O bond. The mechanism by which molecular hydrogen is activated by interaction with a pair of O⁻ ions is discussed in more detail in Sect. 3.3.

The major result from this investigation of a possible lattice parameter, i.e. geometric, effect, is a tentative explanation of the catalytic activity difference experimentally observed between MgO, CaO, and NiO for the H₂-D₂ equilibration reaction.

3.3. Mechanism of Hydrogen Activation on Electron Defect Sites at the Surface of MgO

A quite pictorial way of discussing the molecular H₂ activation mechanism is to plot the data summarized in Table 1 as shown in Fig. 5. It represents the variation in the

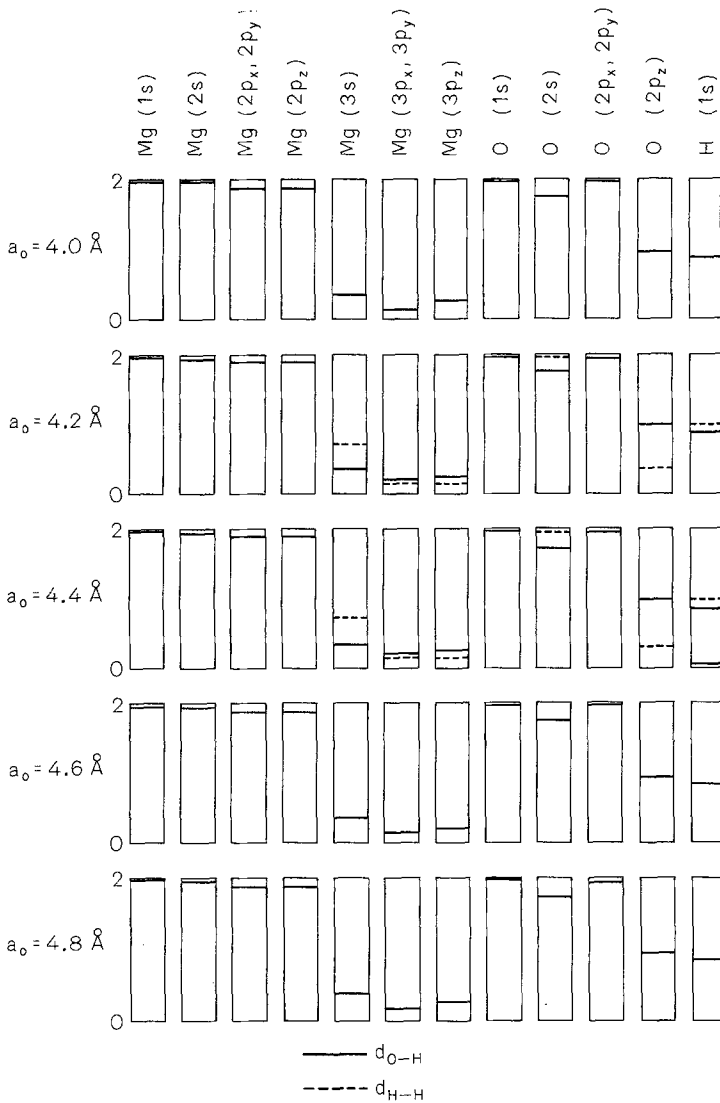


Fig. 4. Electronic populations of the various atomic orbitals of H, O, and Mg as a function of a_0 at the energy minima corresponding to chemisorbed H_2 (---) and hydroxyl groups (—)

energy of the various MO's as a function of the OH (or HH) separation when $a_0 = 4.2 \text{ \AA}$, i.e. the bulk lattice parameter of MgO. We will only consider the valence MO's namely $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $1\pi_u$ and $1\pi_g$.

As R decreases the two hydrogen atoms are moving symmetrically apart from the central magnesium vacancy, thereby simulating the progressive dissociation of the hydrogen molecule.

The position of the core level orbitals is almost unaffected. Hence, they will not be considered further.

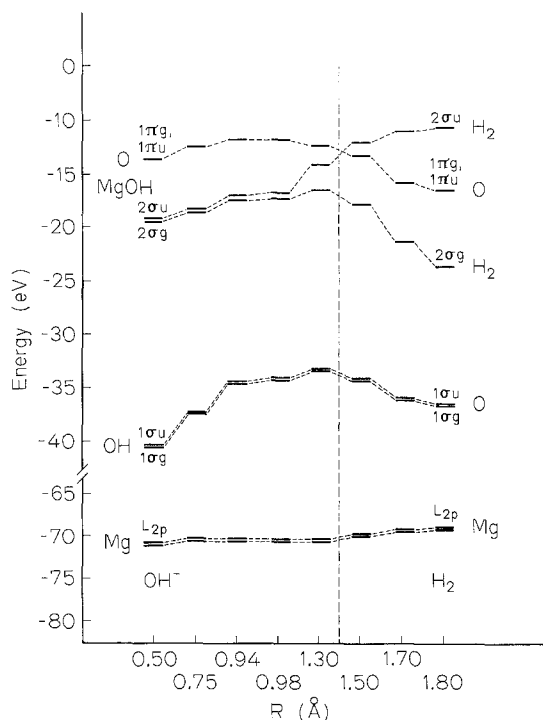


Fig. 5. Energy variation of the various molecular orbitals as a function of R ($a_0 = 4.2 \text{ \AA}$)

The $1\sigma_g$ orbital, which for $R > 1.5 \text{ \AA}$ is essentially the O(2s) atomic orbital, becomes for decreasing R values a MO which is bonding between O and H and slightly bonding between the two hydrogen atoms.

A fairly similar variation is observed for the $1\sigma_u$ orbital but it leads, at small R values, to a molecular orbital which is bonding between O and H and antibonding in the inter-hydrogen region.

The $1\pi_g$ and $1\pi_u$ MO's are respectively bonding and antibonding. They arise from the combination of the $2p_x$ and $2p_y$ atomic orbitals of oxygen with the $3p_x$ and $3p_y$ orbitals of magnesium. A maximum in the energy of these is observed for $R = 1.4 \text{ \AA}$, a distance which corresponds to the intermediate energy maximum in the total energy curve (see Fig. 3).

The behavior of the $2\sigma_g$ and $2\sigma_u$ orbitals is most interesting. For values of R greater than 1.5 \AA , the $2\sigma_g$ MO is bonding between the two hydrogens, and slightly antibonding between the H(1s) and the O($2p_z$) and the H(1s) and O(2s) orbitals respectively. It is essentially a combination of the H(1s) molecular orbitals. When R decreases, the bonding character between the H atoms also decreases while an increased contribution of O($2p_z$) and Mg(3s) takes place. This $2\sigma_g$ MO then becomes bonding for Mg(3s) and O(2s), O($2p_z$) and H(1s), and slightly antibonding between H(1s) and O(2s). An energy maximum is also observed for $R = 1.4 \text{ \AA}$.

For R values greater than 1.5 Å, the $2\sigma_u$ MO lies above the 1π levels. It has an antibonding character between the H atoms, while it is bonding for H(1s) and O($2p_z$), and H(1s) and O(2s). It has a small antibonding character between Mg(3s) and O(2s). The major atomic contributions (in terms of the LCAO coefficients) are in this case H(1s), O($2p_z$), and Mg(3s). The energy of this orbital uniformly decreases with decreasing R values leading to a 2σ degenerate energy level at very small R values. This $2\sigma_u$ MO is then delocalized over the whole system, being antibonding between the two H(1s) orbitals and the H(1s) and O(2s) orbitals, and bonding between H(1s) and O($2p_z$) as well as Mg(3s) and O(2s). The latter character predominates. Let us also point out that this level crosses the $1\pi_u$ and $1\pi_g$ levels when R is about equal to 1.5 Å.

This detailed analysis of the behavior of the various MO's as a function of R shows that in the "chemisorbed hydrogen" region ($R > 1.5$ Å) the $2\sigma_g$ and the $2\sigma_u$ orbitals can be considered as the bonding and antibonding orbitals, respectively, of molecular hydrogen. The $1\sigma_g$ and $1\sigma_u$ orbitals are essentially bonding between Mg and O. The overall system can hence be schematized as the addition of one hydrogen molecule to two MgO^+ ($\text{Mg}^{2+} + \text{O}^-$) entities. Then, it is not surprising that, for $R = 1.698$ Å (which corresponds to the H-H optimized equilibrium distance), the energy separation between the $2\sigma_u$ and $2\sigma_g$ orbitals is of 10.2 eV, a value which compares closely to 9 eV, which is the known separation between the σ bonding and σ^* antibonding MO for the free hydrogen molecule.

At low R values ($R < 1.5$ Å) the $1\sigma_g$ and $1\sigma_u$ MO's are bonding for the hydroxyl group while the $2\sigma_g$ and $2\sigma_u$ MO's are bonding for Mg and O. The formal description of the system is then (2MgOH^+), or $2\text{Mg}^{2+} + 2\text{OH}^-$.

In conclusion, when molecular hydrogen is chemisorbed on an O^- -ion pair, in the immediate neighborhood of a magnesium ion vacancy, the activation and subsequent dissociation of the hydrogen molecule is due to a decrease of the $2\sigma_g$ MO bonding character between the H atoms, while at the same time the $2\sigma_u$ MO, which was initially antibonding between Mg and O, becomes a bonding MO. The bonding character of the $1\sigma_g$ and $1\sigma_u$ MO's between O and H uniformly increase. The combination of these three effects result in the splitting of the hydrogen molecule.

4. Conclusions

This theoretical study, by the molecular orbital method in its non-empirical formulation, of the system $(\text{MgOHV}_{\text{Mg}}\text{HOMg})^{2+}$ which is used to simulate the defect surface of MgO has enabled us to show that:

- a) a stable state of chemisorbed molecular hydrogen was present when the lattice parameter (the O-O separation) was of 4.2–4.4 Å;
- b) activation with dissociation of the chemisorbed hydrogen molecule was likely to take place with a relatively small activation energy;
- c) the catalytic activity difference between MgO and CaO, for the H_2 - D_2 isotopic exchange reaction conducted at low temperature was probably resulting from a geometric effect: an increase of the lattice parameter leading to a rapid increase of the activation energy.

A mechanism is proposed for the activation of molecular hydrogen on such defect oxidic surface which is not so different from that proposed in the case of transition metal complexes. Indeed, in the latter case it is known that H_2 activation can occur in two different ways. First, H_2 can act as an electron donor and the bonding electrons of the H_2 molecule are transferred primarily to vacant d orbitals of the metal ion [19]. The second possibility considers the electron transfer of an electron from the metal atom to an antibonding orbital of the hydrogen molecule, i.e. H_2 acts as an electron acceptor [20]. Our results clearly indicate that, in the present case, H_2 behaves as an electron donor (see Fig. 2) and that its activation is due to the decrease of the bonding character of the $2\sigma_g$ orbital which is essentially the σ bonding orbital of molecular hydrogen. The $2p_z$ orbitals of the two nearby O^- ions play, in the present case, a role very similar to that of a vacant d orbital in a transition metal ion.

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