Energy-level alignment in the adsorption of phosphonyl reagents on $\gamma$-Al$_2$O$_3$

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**Abstract**

Density functional theory is applied to the computation of the adsorption energy ($\Delta E_{\text{ads}}$) for a series of molecules on $\gamma$-Al$_2$O$_3$. Three different cluster models are used to represent the $\gamma$-Al$_2$O$_3$ surface. The molecules of interest all contain a phosphonyl (P=O) functional group and adsorb via formation of a donor bond between the O atom and a threefold-coordinated tetrahedral Al [Al(Td)] surface site. The highest occupied molecular orbital (HOMO) of the free molecule is, in all cases, composed largely of non-bonding orbitals on the coordinatively-unsaturated Al(Td) site and constitutes a surface state. A linear relationship is found between $\Delta E_{\text{ads}}$ and the difference between the orbital energies of the molecular HOMO (e$_{\text{m}}$) and the surface state (e$_{\text{s}}$). Trends in $\Delta E_{\text{ads}}$ for different molecules can then be understood in terms of variations in e$_{\text{m}}$. Likewise, differences in $\Delta E_{\text{ads}}$ for various cluster models can be explained by considering the differences in the predicted e$_{\text{s}}$ values. A further evaluation of the cluster models is presented by comparing results for the physisorption of H$_2$O or CO with those obtained from two-dimensionally-periodic slab models. When differences in e$_{\text{m}}$ and e$_{\text{s}}$ are accounted for, the various models and computational procedures are seen to yield essentially equivalent results for adsorption of the molecules considered. These results are thought to constitute a useful conceptual tool for rationalizing $\Delta E_{\text{ads}}$ values for different molecules and cluster models.

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1. Introduction

Many highly toxic chemicals involve the phosphonyl (P=O) functional group. These include herbicides and pesticides as well as chemical warfare agents (CWAs) such as Tabun (GA), Sarin (GB), Soman (GD) and VX. The adsorption of these species on various substrates is an important issue in “agent fate”, i.e., the stability of the adsorbate with respect to desorption, decomposition and reaction with environmental species. In both experiment [1,2] and theory [3–6], adsorption on the surface of a Lewis-acid material reaction with environmental species. In both experiment [1,2] and theory [3–6], adsorption on the surface of a Lewis-acid material...
Density functional theory is applied to the computation of the adsorption energy (DEads) for a series of molecules on c-Al2O3. Three different cluster models are used to represent the c-Al2O3 surface. The molecules of interest all contain a phosphonyl (P@O) functional group and adsorb via formation of a donor bond between the O atom and a threefold-coordinated tetrahedral Al [Al(Td)] surface site. The highest occupied molecular orbital (HOMO) of the free molecule is, in all cases, composed largely of non-bonding orbitals on the O atom of the P@O group. The empty ??dangling orbital? on the coordinatively-unsaturated Al(Td) site constitutes a surface state. A linear relationship is found between DEads and the difference between the orbital energies of the molecular HOMO (eH) and the surface state (eS). Trends in DEads for different molecules can then be understood in terms of variations in eH. Likewise, differences in DEads for various cluster models can be explained by considering the differences in the predicted eS values. A further evaluation of the cluster models is presented by comparing results for the physisorption of H2O or CO with those obtained from two-dimensionally-periodic slab models. When differences in eH and eS are accounted for, the various models and computational procedures are seen to yield essentially equivalent results for adsorption of the molecules considered. These results are thought to constitute a useful conceptual tool for rationalizing DEads values for different molecules and cluster models.
2.2. Bulk and two-dimensionally-periodic slab models for $\gamma$-$\text{Al}_2\text{O}_3$

Calculations for bulk $\gamma$-$\text{Al}_2\text{O}_3$ and for a two-dimensionally periodic slab (2-DPS) were done using the Crystal 03 suite of programs [15,16] in order to study surface states. The B3LYP hybrid functional was used due to its demonstrated [17] ability to give band gaps in good agreement with experiment for a wide range of materials including $\text{Al}_2\text{O}_3$. All-electron Gaussian basis sets [15] for Al and O, designated 8-21d1G (or 86-21G(d)) and 8-411d11G (or 8-411G(2d)), respectively, were used without modification to construct Bloch functions. The $k$-point sampling used an $8 \times 8 \times 8$ ($8 \times 8 \times 1$) grid for the bulk (2-DPS) and an “extra-large” (75,974) DFT integration grid. In Crystal, truncation of the sums of Coulomb and exchange terms in the Fock matrix is determined by five overlap criteria (T1–T5) [15,16]. These were set at $10^{-7}$ for T1–T4 and $10^{-14}$ for T5. In the multipolar expansion zone [15,16] a maximum order of $L = 6$ was used.

The $\gamma$-$\text{Al}_2\text{O}_3$ model used here is the defective-spinel structure given by Pinto et al. [18] on the basis of plane-wave pseudopotential LDA calculations. The bulk- (and thus the surface-) structure of $\gamma$-$\text{Al}_2\text{O}_3$ is a subject of controversy [18–29], the essential aspects of which are summarized elsewhere [30–32]. Realistic models of high-surface-area $\gamma$-$\text{Al}_2\text{O}_3$ powders, even in the absence of hydroxylation, may involve a wide variety of different Al and O surface sites as discussed in, for example, Ref. [33]. The choice of bulk model and surface plane determines the distribution and identity of potential reactive sites. For example, the (100) surface of the non-spinel model [22] exposes three inequivalent fivefold-coordinated $\text{Al(O}_h\text{)}$ sites, each with a different chemical character. The present work focuses on one particular type of surface site; namely, the threefold-coordinated $\text{Al(T}_d\text{)}$. This is most easily modeled (see below) using the (111)a surface of the defective-spinel structure [18] but also occurs on the (110) surface of the non-spinel model [22]. Hence, the present work is primarily a study of adsorption at threefold-coordinated $\text{Al(T}_d\text{)}$ sites rather than on a particular surface plane of a specific bulk-lattice model. It will be shown below that the essential difference among these models lies in the energies of the empty surface states derived from cations.

In the present work, the lattice constants were kept fixed at the optimized bulk values [18] while the atom positions were allowed to vary in a geometry optimization of the bulk structure. Only very small differences (<0.002 Å) were found between the fractional atom positions and those of the initial structure [18]. A (1 × 1) slab unit cell was used with a thickness of 31 atomic layers (equivalent to one crystallographic unit cell) and the (111)a plane as the surface layer. The slab unit cell was symmetric about the mid-plane so that no dipole potential was generated. The (111)a, which has been identified [18] as the most stable surface of a bulk single crystal, consists of singly-unoccupied tetrahedral $\text{Al(T}_d\text{)}$ sites and two types of O sites. One is threefold-coordinated in the bulk, as a result of being adjacent to a vacant octahedral $\text{Al(O}_h\text{)}$ spinel site, and remains so at the surface. This O has one $\text{Al(T}_d\text{)}$ and two $\text{Al(O}_h\text{)}$ nearest-neighbors. The other O is fourfold-coordinated in the bulk but is missing its $\text{Al(T}_d\text{)}$ nearest-neighbor at the surface. The $\text{Al(T}_d\text{)}$ is a strong Lewis-acid site on the $\gamma$-$\text{Al}_2\text{O}_3$ surface [22,34], and there are no unsaturated $\text{Al(O}_h\text{)}$ sites on the (111)a surface. Upon relaxing the slab, with the lattice constants fixed but all atoms unconstrained, it was found that the atomic displacements were small (<0.1 Å) beyond the outermost few planes, in agreement with previous results [18].

2.3. Cluster models for $\gamma$-$\text{Al}_2\text{O}_3$

Three different cluster models (Fig. 2) were used, all of which are described in detail elsewhere [3,4]. All are derived from the (111)a defective-spinel surface discussed above. One is an $\text{Al}_2\text{O}_3\text{Cl}_x$ structure with unsaturated edge atoms [3], and the others are $\text{Al}_3\text{O}_{12}$ and $\text{Al}_{32}\text{O}_{48}$ clusters with pseudo-hydrogen termination (PHT) [4,35]. A pseudo-hydrogen (PH) is a neutral atom with a non-integral nuclear charge and electron occupancy. Each PH supplies to a coordinatively-unsaturated Al or O the amount of charge that would be derived from the missing nearest-neighbor in the $\gamma$-$\text{Al}_2\text{O}_3$ lattice. Due to the presence of both four and sixfold-coordinated Al atoms, four different PHs are needed which are shown in Fig. 2b as H$_{1/2}$, etc. An H$_{1/2}$, for example, has a nuclear charge of +1/2 [e] and an electron occupancy of −1/2 [e]. H$_{1/2}$ and H$_{3/4}$ are used to terminate O atoms, and H$_{5/4}$ and H$_{3/2}$ are used to

Fig. 1. Molecular structures for TCPO, DMMP, Sarin and TMPO. The Sarin enantiomer was arbitrarily chosen.
B3LYP, functional. For continuity with previous work [3], calculations were done using the (VWN + PBE), rather than the use of PHs) and the TZP basis sets described above. For technical reasons these were done with 3-21G basis sets. The Al\(_{20}O_{30}\) \(\Delta E_{ads}\) results obtained here for Sarin and DMMP (see below) differed by <1 kcal/mol from previous results [3] obtained using 6-311G(df) basis sets for the molecule and the Al(–O–)\(_3\) site. The Al\(_{20}O_{30}\) results showed both internal and spin-restricted/spin-unrestricted instabilities [13] due to the unsaturated edge atoms. Reoptimizing the wavefunction to eliminate these instabilities lowered the total energy (with or without adsorbates) by about 3 kcal/mol. In computing \(\Delta E_{ads}\) this effect approximately cancelled, leading to a net reduction in adsorption energy of only ~0.4 kcal/mol relative to the uncorrected result.

Geometry optimization began, for the bare clusters, with keeping all other Al and O atoms fixed in the ideal-lattice positions. For adsorption the PHs remained fixed in the optimized positions while atoms in the molecule and in the Al(–O–)\(_3\) adsorption site were allowed to vary. Optimizations involving Al\(_{20}O_{12}\) were done using the same convergence criteria as for the free molecules (see above). For Al\(_{32}O_{48}\) the convergence criteria were relaxed to the ADF defaults. For consistency in obtaining \(\Delta E_{ads}\) the same criteria were used for all three components (adsorbate + cluster, bare cluster and free molecule).

Vibrational normal modes were also obtained for adsorbates on the Al\(_{32}O_{48}\) and Al\(_{20}O_{12}\) (PHT) clusters. Due to the large number of atoms involved this was not attempted for the Al\(_{32}O_{48}\) (PHT) cluster. The interest here is in the internal modes of the molecule, particularly in \(v(P-O)\), the frequency of the P–O stretching vibration. These receive little or no contribution from displacements of atoms in the cluster itself (including the PHs). Hence, the results are considered to be reliable even though only partial geometry optimizations are performed, as noted above.

3. Results

3.1. Free-molecule structures, vibrational frequencies and ionization potentials

Table 1 shows computed structural parameters for the free molecules together with data for TCPO from microwave (\(\mu\)-wave) spectroscopy [36] and for TMPO from X-ray crystallography [37]. To our knowledge, no corresponding structural parameters are available

<table>
<thead>
<tr>
<th></th>
<th>(r(P-O)) [(\text{Å})]</th>
<th>(r(P-X)) [(\text{Å})]</th>
<th>(\angle(O-P-X)) [°]</th>
<th>(\angle(X-P-X)) [°]</th>
<th>(v(P-O)) [(\text{cm}^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCPO(^\text{a})</td>
<td>1.455</td>
<td>1.989</td>
<td></td>
<td></td>
<td>103.7</td>
</tr>
<tr>
<td></td>
<td>1.462 (1.474)</td>
<td>2.042 (2.030)</td>
<td>114.9 (114.6)</td>
<td>103.5 (103.9)</td>
<td>1268 (1274)</td>
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<tr>
<td>Sarin</td>
<td>1.473 (1.481)</td>
<td></td>
<td></td>
<td></td>
<td>1311</td>
</tr>
<tr>
<td>DMMP</td>
<td>1.482 (1.490)</td>
<td></td>
<td></td>
<td></td>
<td>1256 (1250)</td>
</tr>
<tr>
<td>TMPO(^\text{b})</td>
<td>1.489</td>
<td>1.771</td>
<td>112.8</td>
<td>105.9</td>
<td>1148</td>
</tr>
<tr>
<td></td>
<td>1.498 (1.503)</td>
<td>1.830 (1.829)</td>
<td>114.1 (113.9)</td>
<td>104.4 (104.7)</td>
<td>1178 (1193)</td>
</tr>
</tbody>
</table>

\(^{a}\) Observed values are italicized. Non-italicized values are computed. The first value is at the B3LYP/6-311G(d) level, and the value in parentheses is at the (VWN + PBE/TZP) level. \(X = \text{Cl}\) for TCPO and \(\text{CH}_3\) for TMPO. Bond lengths are in Angstroms, and bond angles are in degrees. No experimental structural parameters are available for DMMP or Sarin.

\(^{b}\) \(v(P-O)\) is in \(\text{cm}^{-1}\). The experimental values for TCPO [43], DMMP [44] and Sarin are from gas phase infrared spectra. The TMPO value is for the solid [45]. The Sarin value is an estimate [3] based on data for the liquid [2]. Calculated values all pertain to the gas phase.

\(^{c}\) Experimental structural parameters are from Ref. [36].

\(^{d}\) No experimental value is given.

\(^{e}\) Experimental structural parameters are given in Ref. [37]. In the crystal one \(\text{C}\) atom lies in a mirror plane together with the \(P-O\) group and is, therefore, inequivalent to the other \(\text{C}\) atoms which lie above or below the plane. This slight inequivalence is ignored in the table, and the experimental values given are averages over all \(\text{CH}_3\) groups.
for either DMMP or Sarin; although, moments of inertia are available from \( \mu \)-wave data [38,39]. Generally good agreement is seen between the two different calculations and between observed and calculated values for TCPO and TMPO.

Sarin and DMMP exhibit different conformers which have been studied using \( \mu \)-wave spectroscopy and \textit{ab initio} or semi-empirical theory [38–42]. In the present work the free molecules, upon geometry optimization, relaxed into the lowest-energy conformations as reported previously [38–40] and shown in Fig. 1. For Sarin, calculations of the relaxed total energy vs. the angle of rotation of the \((\text{CH}_3)_2\) group about the \(C–O\) bond were done in 10° steps at both the \((\text{VWN} + \text{PBE})/\text{TZP}\) and \text{B3LYP}/6-311G(d) levels. The results (not shown) were very similar to those obtained previously [40] at the \text{B3LYP}/6-31G(d,p) level.

Table 1 also shows observed and calculated values for \(\nu(P=0)\), which is sensitive to adsorption (see below). The experimental values for TCPO [43], DMMP [44] and Sarin (an estimate [3] based on data for the liquid [2]) are all for the gas phase and can be compared directly with the computed results. On the other hand TMPO is a solid, and infrared data were obtained for a powder dispersed in mineral oil [45]. \(\nu(P=0)\) is known to be significantly red-shifted in the condensed phase due to intermolecular interactions, which are not included in the calculation. For example, \(\nu(P=0)\) is 31 cm\(^{-1}\) lower in liquid vs. gas-phase DMMP [44]. Except for solid TMPO, the experimental results are consistently 51 ± 4 cm\(^{-1}\) higher than the calculated values. This suggests a systematic error in the calculation which should cancel, approximately, in obtaining \(\Delta\nu(P=0)\), the shift caused by adsorption. It was also found that \(\nu(P=0)\) for free Sarin is essentially independent of conformation. At the \text{B3LYP}/6-311G(d,p) level a difference of only about 4 cm\(^{-1}\) was found between the lowest-energy (“Sarin-I”) and highest-energy (“Sarin-III”) conformations as defined in Ref. [40].

The orbital energies of the molecular HOMOs are needed in the following discussion. Since these bear some relation to experimentally-observable IPs these quantities have been computed for the free molecules. Table 2 shows the VIP and AIP results, together with the HOMO orbital energies for the neutral species. The VIPs can be compared directly with PES data [46,47] which show better agreement in the case of \text{B3LYP}/6-311G(d). For \text{B3LYP} the largest discrepancy between experiment and calculation (0.54 eV) is for DMMP, which is chemically similar to Sarin. Correcting the computed VIP for Sarin (10.60 eV) by this amount leads to an estimate of about 11.14 eV for the actual VIP.

For TCPO and TMPO the HOMO is twofold degenerate, with large contributions from \(p_x\) and \(p_y\) NBOs on the O atom of the \(P=0\) group (which is aligned along the \(z\)-axis). For Sarin and DMMP the degeneracy is lifted with splittings of about 0.05 and 0.09 eV, respectively, between the HOMO and HOMO-1. This effect is neglected in Table 2 which gives IPs derived from ionization of the HOMO. All quantities show the same trend, decreasing in magnitude monotonically in the order \(\text{TCPO} > \text{Sarin} > \text{DMMP} > \text{TMPO}\). This reflects the inductive effect of strongly- vs. weakly-electronegative species (e.g., Cl vs. \(\text{CH}_3\)) on the P atom and, in turn, on the HOMO energy. It is noted in passing that, in computing the AIP, a Jahn–Teller distortion (which breaks the \(C_3\) symmetry) was found for the TCPO and TMPO cations. Further discussion of this aspect is beyond the scope of the present work.

### 3.2. \(\gamma\)-\(\text{Al}_2\text{O}_3\) \(\text{Al}(T_d)\) surface state

Empty surface states can be identified using electron energy loss spectroscopy (ELS). As in optical absorption, the transition energy includes the effect of electron–hole interaction and thus provides only a lower limit on the separation between the initial and final levels in the electronic ground state. Inverse photoemission spectroscopy [48] or tunneling spectroscopy can also be used to study empty surface states, without the perturbing effects of core or valence holes, but such data are not to our knowledge available for \(\gamma\)-\(\text{Al}_2\text{O}_3\).

One ELS experiment was reported [49] for a \((111)\)-oriented \(\gamma\)-\(\text{Al}_2\text{O}_3\) film grown by thermal oxidation of a NiAl (110) surface. No surface states were seen in the band gap. However, the \((111)\) surface in this case is believed [50] to be O-terminated and, hence, would not be expected to show empty Al-derived surface states. Ultra-thin \(\gamma\)-\(\text{Al}_2\text{O}_3\) films have been formed by oxidation of a \(\text{Ni}_3\text{Al}(100)\) surface [51]. These show a band gap of \(E_g = 4.3\) eV, much smaller than that for defect-free bulk \(\gamma\)-\(\text{Al}_2\text{O}_3\) (\(E_g = 7.2\) eV [52]). This was ascribed to the presence of defects, and in any case, such ultra-thin oxide films may not be representative of the bulk material [53]. Thus the experimental situation regarding empty surface states on \(\gamma\)-\(\text{Al}_2\text{O}_3\) is uncertain at present.

A theoretical study has been performed [18] for various \(\gamma\)-\(\text{Al}_2\text{O}_3\) surfaces using plane-wave pseudopotentials and a 2-DPS model based on the defective-spinel structure. The computed bulk band gap (\(E_g = 3.97\) eV) underestimates the experimental value, as is typical in LDA calculations [54]. On the \((111)\) surface the valence band maximum (VBM) is found to move down, and the conduction band minimum (CBM) to move up, relative to the respective bulk band edges which leads to a surface band gap of about 4.7 eV. On this surface, a narrow band of states derived from empty \(\text{Al}(T_d)\) orbitals is found at about 1.3 eV below the surface CBM. Similar calculations have been done for the \((100)\) and \((110)\) surfaces of the non-spinel structure [22]. These also show distinct surface-state features near the CBM which are assignable to each of the different unsaturated Al sites.

To obtain an independent assessment of the surface-state energy, calculations were performed for the bulk lattice and for the 2-DPS as described above. For the bulk lattice an \(E_g\) of 6.2 eV was found which is in fair agreement with experiment (\(E_g = 7.2\) eV [52]). A previous \text{B3LYP} treatment for an unspecified form of \(\text{Al}_2\text{O}_3\) (presumably \(\alpha\)-\(\text{Al}_2\text{O}_3\)) gave a bulk \(E_g\) of 8.5 eV [17] vs. the experimental \(\alpha\)-\(\text{Al}_2\text{O}_3\) value of 8.8 eV [52]. Fig. 3 shows the density of states for the 2-DPS in the vicinity of the band edges. A surface \(E_g\) of about 7.0 eV is found with the lowest-energy surface-state (51) located just below (within ~0.5 eV from) the CBM. A second surface state (52), also derived from surface \(\text{Al}(T_d)\) sites, is found at

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated HOMO energies ((\epsilon_{\text{HOMO}})) and ionization potentials (eV) for free molecules*</td>
</tr>
<tr>
<td><strong>HOMO energy ((\epsilon_{\text{HOMO}}))</strong></td>
</tr>
<tr>
<td>TCPO</td>
</tr>
<tr>
<td>Calculated (vertical IP)</td>
</tr>
<tr>
<td>Calculated (adiabatic IP)</td>
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<td>Experimental (vertical IP)</td>
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</table>

* Values not in parentheses are calculated at the B3LYP/6-311G(d) level. Values in parentheses are calculated at the (VWN + PBE)/TZP level.

\(^a\) From PES data, Ref. [46].

\(^b\) No experimental value is available. For Sarin, a VIP of 11.14 eV is estimated (see text) based on the DMMP results.

\(^c\) From PES data, Ref. [47].
about 4.8 eV above the CBM. The larger $E_g$ for the slab vs. the bulk lattice is consistent with previous results [18]. The position of S1 is essentially in agreement with that given previously [18]; although, the present work finds it lying somewhat closer to the CBM.

It now remains to be seen how closely the various cluster models reproduce the 2-DPS S1 position. The Al$_8$O$_{12}$ cluster (with PHT) gives a “band gap” of about 4.4 eV. This is taken as the energy difference between the HOMO and the lowest-energy virtual state not receiving any substantial contribution from atomic orbitals localized on the unsaturated Al(T$_d$) “surface” cation. The “surface state” associated with this site then falls at about 1.0 eV below the CBM. The larger $E_g$ for the slab vs. the bulk lattice is consistent with previous results [18]. The position of S1 is essentially in agreement with that given previously [18]; although, the present work finds it lying somewhat closer to the CBM.

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3.3. Energy level alignment

It is now necessary to define a common reference for the energy levels of the cluster and the molecule. Formation of the dative bond (see below) involves the transfer of only a small amount of charge (~0.1–0.2|e|) from the P=O group to S1. Hence, it is meaningful to consider the chemical potential of an electron in the HOMO or in S1. Janak [56] has shown that $\epsilon_s = E_i|\\Omega|$, where $\epsilon_s$ is the DFT energy of orbital (i) and $n_\Omega$ is the orbital population (treated as a continuous variable in DFT). For a non-metallic system, in which many-body screening effects can be neglected, $\epsilon$ is effectively the total energy. Therefore in the following discussion $\epsilon_s$, the DFT orbital energy of the free-molecule HOMO, is taken as the chemical potential of an electron in the HOMO. Likewise $\epsilon_s$, the DFT orbital energy of S1, is taken as the chemical potential of an electron in the surface state. The resulting $\epsilon_s$ and $\epsilon_o$ values are summarized in Table 3 and shown schematically in Fig. 3.

An electron affinity of $\gamma \approx 1$ eV, which places the CBM relative to vacuum (cf. Fig. 3), has been estimated [57] for $\gamma$-Al$_2$O$_3$. A $\gamma$ of 1.35 eV has been estimated [58] for $\gamma$-Al$_2$O$_3$ on the basis of electron tunneling measurements [59] on an ultra-thin film on NiAl(110) [50]. As noted above, such films may not be characteristic of the bulk material. If one assumes, nevertheless, that $\gamma$ is slightly larger than 1 eV for $\gamma$-Al$_2$O$_3$ and places S1 within ~0.5 eV of the CBM, as found in the present 2-DPS results, then $\epsilon_o \approx 1.5$ eV is obtained as an estimate for the actual value. This is close to the Al$_{12}$O$_{48}$ result of 1.40 eV. Hence one expects, $a$ priori, that the Al$_{12}$O$_{48}$ cluster will provide the most accurate model of the active site on the defective-spinel (111)α surface, a view which will be supported by results given below.

### Table 3

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
<th>$\chi$</th>
<th>$\epsilon_{\text{HOMO}}$</th>
<th>$\epsilon_{\text{VBM}}$</th>
<th>$\epsilon_s$</th>
<th>$\epsilon_o$</th>
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</thead>
<tbody>
<tr>
<td>TCPO</td>
<td>$-33.3$</td>
<td>9.51</td>
<td>$-33.0$</td>
<td>$-24.7$</td>
<td>8.04</td>
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<tr>
<td>Sarin</td>
<td>$-49.0$</td>
<td>8.30</td>
<td>$-51.5$</td>
<td>$-39.8$</td>
<td>6.98</td>
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<tr>
<td>DMMP</td>
<td>$-57.2$</td>
<td>7.82</td>
<td>$-53.0$</td>
<td>$-41.4$</td>
<td>6.53</td>
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<tr>
<td>TMPO</td>
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<td>7.19</td>
<td>$-58.6$</td>
<td>$-51.2$</td>
<td>5.93</td>
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</tr>
<tr>
<td>DMMP</td>
<td>$-4.01$</td>
<td>2.18</td>
<td></td>
<td></td>
<td>1.40</td>
<td></td>
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</tbody>
</table>

* All energies are kcal/mol and have been corrected for BSSE. BSSEs computed for Al$_2$O$_3$ was also used for Al$_{12}$O$_{48}$ since the adsorption geometry and computational conditions are essentially the same in both cases.

* Results for Al$_2$O$_{48}$ (no PHT) obtained at the B3LYP/6-311G(d) level and corrected for the effects of wavefunction instabilities (see text).

* HOMO orbital energies calculated at the B3LYP/6-311G(d) level, from Table 2.

* Results for Al$_{12}$O$_{48}$ and Al$_{12}$O$_{48}$ (both PHT-terminated) obtained at the (VWN + PBE)/TZP level.

* Surface state (S1) orbital energy determined as described in the text. A positive value indicates that S1 lies below the vacuum level.
3.4. Adsorption energies, geometries and vibrational frequencies

The main theme of this work is the dependence of $\Delta E_{\text{ads}}$ on $4_{41}$ and $5_s$. The essential results are summarized in Table 3. Fig. 4a shows, as an example, the optimized structure of TMPO adsorbed on the Al$_8$O$_{12}$ cluster (with the PHs removed for clarity). For other adsorbates the structure is similar in appearance (e.g., Ref. [3]). For a given cluster, comparing results for different molecules shows the correlation between $\Delta E_{\text{ads}}$ and $4_{41}$. As one expects intuitively on the basis of the frontier-orbital concept [7–9], decreasing $4_{41}$ makes charge transfer easier and leads to an increased $\Delta E_{\text{ads}}$. For a given molecule, comparing results for the Al$_8$O$_{12}$ vs. Al$_{12}$O$_{48}$ clusters shows the correlation between $\Delta E_{\text{ads}}$ and $5_s$. Again as expected, moving S1 up toward vacuum makes the surface less acidic (i.e., a weaker acceptor) and impedes dative-bond formation, thus decreasing the magnitude of $\Delta E_{\text{ads}}$.

Fig. 5 shows plots of the results in Table 3. All clusters yield an essentially linear dependence of $\Delta E_{\text{ads}}$ on $(4_{41}-5_s)$ with slightly different parameters for Al$_{20}$O$_{30}$ vs. Al$_{8}$O$_{12}$ and Al$_{12}$O$_{48}$. Initially the Al$_8$O$_{12}$ and Al$_{12}$O$_{48}$ results were fitted separately, but the fits were virtually indistinguishable and Fig. 5 shows a single fit for both. The reason for the small differences between the PHT and non-PHT parameters (about 5% in the slope and 2% in the intercept) is difficult to identify. One possibility is the different DFT functionals used for the two sets of calculations.

Although the qualitative dependence of $\Delta E_{\text{ads}}$ on $4_{41}$ and $5_s$ is expected, the quantitatively linear behavior in Fig. 5 is not. A linear combination of atomic orbitals (LCAO) treatment (e.g., Refs. [7,9]) yields $\Delta E_{\text{ads}} = H^2/\Delta \epsilon$ where $H$ is the interaction energy between the empty S1 state and the doubly-occupied molecular HOMO and $\Delta \epsilon = 5_s - 4_{41}$. This is based on a perturbation approximation ($|H| \ll |\Delta \epsilon|$) which does not apply in the present case since, for the $\Delta E_{\text{ads}}$ and $\Delta \epsilon$ values encountered here, $H$ and $\Delta \epsilon$ would be of similar magnitude. Fits to $\Delta E_{\text{ads}}$ which were linear in $1/\Delta \epsilon$ (not shown) were not quite as good as those in Fig. 5. Different fits were obtained for Al$_8$O$_{12}$ and Al$_{12}$O$_{48}$ when plotting vs. $1/\Delta \epsilon$, with correlation coefficients of $r = 0.931, 0.967$ and 0.981 for Al$_{20}$O$_{30}$, Al$_{12}$O$_{48}$ and Al$_8$O$_{12}$, respectively.

When the effects of $4_{41}$ and $5_s$ are “factored out”, similar behavior is seen for different cluster models, functionals and basis sets. With all else equal, differences in $\Delta E_{\text{ads}}$ for various clusters can be traced primarily to differences in $5_s$. Previous 2-DPS results for the Al$_8$O$_{12}$ (PHT) cluster. It was also found that the strength of the interaction of CO with these sites, as measured by $\Delta E_{\text{ads}}$ and by $\Delta \epsilon(C=O)$, correlates with the difference between $5_s$ and $4_{41}$ (the energy of the CO HOMO, i.e., the 5g orbital). A further discussion of these points, including CO adsorption, is given below.

All adsorbates except TCPO show the possibility of H-bonding between H atoms in the alkyl group(s) and O atoms in the Al$_8$O$_{12}$ cluster. This is based on the observation, in the optimized structures, of one or more CH–O distances in the range of 2.1–2.4 Å. Similar effects have been noted in other studies [5,6] of CWA adsorption on ionic oxides. No attempt has been made here to assess the contribution of these effects to $\Delta E_{\text{ads}}$. However, ab initio studies of other systems [60,61] suggest that such CH–O bonds are weak, with a bond energy of at most ~3 kcal/mol.

Cluster models of the sort used here neglect the long-range contribution to the electrostatic potential at the adsorption site that would arise in a semi-infinite lattice. The possibility was considered that a difference in this potential could contribute to the dif-

Fig. 5. Graphical display of the results in Table 3. The linear regressions are given by $\Delta E_{\text{ads}} = -106.2 + 12.22(4_{41}-5_s)$ for Al$_8$O$_{12}$ (circles) and Al$_{12}$O$_{48}$ (squares), $r = 0.984$ $\Delta E_{\text{ads}} = -104.1 + 12.82(4_{41}-5_s)$ for Al$_{20}$O$_{30}$ (triangles), $r = 0.995$ with $\Delta E_{\text{ads}}$ in kcal/mol and $(4_{41}-5_s)$ in eV. The $r$ values are the correlation coefficients. Data points are labeled for Al$_8$O$_{12}$ and appear in the same order for the other plots. The open symbols show $\Delta E_{\text{ads}}$ values computed for CO (see text) which were not included in the linear regression analysis.

Fig. 4. Model showing the optimized structure for (a) TMPO and (b) H$_2$O adsorbed on the Al$_8$O$_{12}$ cluster. The pseudo-Hs have been removed for clarity. In (b) the dashed line shows a hydrogen bond with $r(O-H) = 1.9864$ Å.
ference in $\Delta E_{ads}$ for the various clusters. With the active Al(Td) as the test site (j), the sum of $q_j/r_j$ over all other sites (i) including the PHs gave $-1.232$ and $-1.173|e|/\AA$ for Al8O12 and Al2O48, respectively. Here $q_j$ is the ionic charge computed using the multipole-derived charge (quadrupole), or MDC-Q, method of Swart et al. [62], and $r_j$ is the distance from (j). Likewise the MDC-Q charge on the active Al(Td) site of the bare cluster is similar for Al8O12 (+1.82) vs. Al2O48 (+1.77). For comparison, a Mulliken charge of +1.66 is found for the surface Al(Td) ion in the 2-DPS calculation described above. For the Al20O30 cluster, a Mulliken charge of +1.30 is found for the “surface” Al(Td), which is smaller than the corresponding values given above. However, the sum over all $q_j/r_j$ is $-1.231|e|/\AA$, essentially the same as that found for the other clusters. Hence, the electrostatic environment in the vicinity of the adsorption site is similar for all three clusters; although, it may of course differ from that for a semi-infinite crystal.

Examination of the cluster orbitals shows that adsorption removes S1 from the gap. Bonding orbitals, with large components from the phosphonyl O atom and small contributions from the Al(Td) adsorption site, appear a few eV below the “VBM”. This is direct (theoretical) evidence for the involvement of S1 in the chemisorption process. The MDC-Q results for Al8O12 and Al2O48 show that the charge transferred to the Al atom is the range of $\pm 0.11$ to $-0.21|e|$, depending on the cluster and the adsorbate.

The configuration of the adsorbed Sarin differs slightly from the lowest-energy Sarin-I structure [40] of the gas-phase molecule. For the Al20O30 cluster the isopropyl group rotates about the C–OP bond by about 27° in the direction of Sarin-II; whereas, for the PHT clusters the rotation is by about 13° in the direction of Sarin-III. For all models, Table 4 shows that $r(\text{Al–OP})$ decreases with increasing $\Delta E_{ads}$ as expected. All models yield about the same (Al–O=P) angle for a given molecule except for Sarin where a larger angle is found for Al20O30 (153°) vs. Al8O12 and Al2O48 (131°). This probably results from the different Sarin configurations, noted above, for Al20O30 vs. Al8O12 and Al2O48. The orientation of the isopropyl group for Sarin adsorbed on Al20O30 requires a larger (Al–O=P) angle to avoid steric interaction between one of the CH3 groups and the cluster.

The computed $\Delta \epsilon(\pi=0)$ values for Al8O12 and Al20O30 are in fairly good agreement with each other and (where available) with experimental data except, again, in the case of Sarin for which the Al2O48 result is too large vs. experiment (–66 cm⁻¹ [2,3]). The explanation for this is uncertain at present. It may lie in the different Sarin conformations in the two models; however, as noted above, $\epsilon(\pi=0)$ for free Sarin appears to be essentially independent of conformation. For adsorbed DMMP the computed $\pi=0$ stretch is strongly coupled to modes at 1161 and 1174 cm⁻¹, and $\epsilon(\pi=0)$ is taken as the average of these values.

Results for the gas-phase molecules (Table 1) show the expected decrease in $\epsilon(\pi=0)$ with decreasing bond strength (i.e., with increasing $r(\text{P}=\text{O})$). Table 4 shows that $r(\text{P}=\text{O})$ is in all cases greater for the adsorbed vs. the gas phase, consistent with a weakening of the $\pi=0$ bond. The increase in bond length is small, being in the range of $\Delta r(\pi=0)$ ≈ 0.03 to 0.06 Å, but there does appear to be a rough correlation between $\Delta \epsilon(\pi=0)$ and $\Delta r(\pi=0)$. However, the correlation between $\Delta \epsilon(\pi=0)$ and $\Delta E_{ads}$ is somewhat more tenuous, as is seen by comparing results for TCPO and TMPO. These show essentially identical $\Delta \epsilon(\pi=0)$ values but $\Delta E_{ads}$ values differing by nearly a factor of two. Similar behavior was found previously [63] for the adsorption of TCPO and DMMP on amorphous silica via H-bonding between Si–OH groups and the phosphonyl O atom. A $\Delta E_{ads}$ of $-10.4$ (–20.0) kcal/mol was computed for TCPO (DMMP), but the experimental $\Delta \epsilon(\pi=0)$ values are about $-34$ and $-19$ cm⁻¹, respectively. The reason for this behavior lies in a unique property of TCPO, whereby Cl orbitals are strongly mixed with both the HOMO and the $\pi=0$ orbital. For the other species studied here the HOMO consists almost entirely of orbitals on the O atom of the P=O group. For TCPO, the HOMO and the $\pi=0$ bond are in effect coupled, and perturbation of the former by adsorption then leads to a disproportionately strong effect on the latter and a correspondingly large $\Delta \epsilon(\pi=0)$.

Finally, other possible modes of adsorption were considered, even though experimental data [1,2] for DMMP and Sarin clearly indicate Al–O=P dative bond formation as the energetically-favored process. Adsorption of Sarin on the Al8O12 cluster gave $\Delta E_{ads}$ of $-26.2$ or $-31.0$ kcal/mol, respectively, for bonding between Al and the F or the isopropoxy O atom. These have not been corrected for BSSE, and doing so would reduce the magnitudes by $\sim 2$ kcal/mol. These can be compared with the BSSE-corrected value of $-51.5$ kcal/mol (Table 3) for Al–O=P bonding. These results are consistent with previous results [3] for the Al20O30 cluster. Bonding of TCPO to Al8O12 via an Al–Cl=P bond was also tested. During relaxation the molecule moved away from the surface, and no bond formed. For TCPO a “reverse” dative bond was investigated, wherein an O atom on the Al2O3 surface acts as an electron donor and the P atom acts as an acceptor. This might, in principle, be energetically feasible since the lowest unoccupied molecular orbital of gas-phase TCPO is computed to lie at 3.485 eV below vacuum.

### Table 4

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Adsorbate</th>
<th>$\Delta E_{ads}$</th>
<th>$r(\text{Al–OP})$</th>
<th>$r(\text{Al–O=P})$</th>
<th>$\Delta \epsilon(\pi=0)$</th>
</tr>
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<tbody>
<tr>
<td>Al20O30</td>
<td>TCPO</td>
<td>–33.3</td>
<td>1.862</td>
<td>1.502 (1.462)</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>Sarin</td>
<td>–49.0</td>
<td>1.813</td>
<td>1.505 (1.473)</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>DMMP</td>
<td>–57.2</td>
<td>1.795</td>
<td>1.523 (1.482)</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>TMPO</td>
<td>–62.2</td>
<td>1.799</td>
<td>1.556 (1.498)</td>
<td>131</td>
</tr>
<tr>
<td>Al8O12 (PHT)</td>
<td>TCPO</td>
<td>–33.0</td>
<td>1.887</td>
<td>1.506 (1.474)</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>Sarin</td>
<td>–51.5</td>
<td>1.838</td>
<td>1.521 (1.481)</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>DMMP</td>
<td>–53.0</td>
<td>1.819</td>
<td>1.523 (1.490)</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>TMPO</td>
<td>–58.6</td>
<td>1.815</td>
<td>1.549 (1.503)</td>
<td>129</td>
</tr>
<tr>
<td>Al2O48 (PHT)</td>
<td>TCPO</td>
<td>–24.7</td>
<td>1.948</td>
<td>1.499 (1.474)</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>Sarin</td>
<td>–39.8</td>
<td>1.863</td>
<td>1.513 (1.481)</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>DMMP</td>
<td>–41.4</td>
<td>1.860</td>
<td>1.516 (1.490)</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>TMPO</td>
<td>–51.2</td>
<td>1.841</td>
<td>1.545 (1.503)</td>
<td>129</td>
</tr>
</tbody>
</table>

* In all cases, adsorption is via Al–O=P dative bond formation (cf. Fig. 4). Energies are in kcal/mol, bond lengths in Ångstroms, bond angles in degrees and frequencies in cm⁻¹. The $\Delta E_{ads}$ values repeat those in Table 3.

* Numbers in parentheses are $P=O$ bond lengths computed for the free molecules.

* $\Delta \epsilon(\pi=0)$ is the calculated $\epsilon(\pi=0)$ for the adsorbed species minus the calculated gas-phase value. No experimental $\Delta \epsilon(\pi=0)$ data are available for TCPO or TMPO. For DMMP the experimental result is –66 cm⁻¹ (Ref. [1]). For Sarin the estimated experimental result is –66 cm⁻¹ (Refs. [2,3]).
at the (VWN + PBE)/TZP level. The molecule was initially positioned with P=O bond pointing away from the surface and with the three Cl atoms coplanar with the P atom. The Al$_{32}$O$_{48}$ cluster was used, and the P was positioned above a coordinatively-un satu rated O atom (see above). However, here again the molecule relaxed away from the surface with no bond formation.

3.5. Comparison of 2-DPS and cluster results

There are, to our knowledge, no experimental data giving $\Delta E_{ads}$ for the systems of interest here. It is therefore difficult to assess the absolute accuracy of the results. However, comparison can be made with results for a 2-DPS which is assumed to model the surface of a semi-infinite crystal more accurately than does a finite cluster. One such comparison is for the physisorption of molecular H$_2$O using the same functionals, basis sets, etc. as for the phosphonyl species. In all cases a dative bond (H$_2$O–Al) forms between the O atom and the unsaturated Al(T$_d$) site. A 2-DPS result of $\approx$ 28.1 kcal/mol for the (1 1 1)$\alpha$ surface has been found by Pinto and Elliott [64] using a plane-wave pseudopotential approach. The results obtained here (corrected for BSSE) are $\Delta E_{ads}$ = -40.1, -36.5 and -30.8 kcal/mol, respectively, for the Al$_{12}$O$_{30}$, Al$_{21}$O$_{12}$ (PHT) and Al$_{12}$O$_{48}$ (PHT) clusters. Again, $\Delta E_{ads}$ decreases in magnitude as $\epsilon_S$ shifts toward vacuum. The Al$_{12}$O$_{48}$ result is close to that found for the 2-DPS which suggests that this cluster, of the three used here, gives the most reliable absolute values for $\Delta E_{ads}$ in comparison to the (1 1 1)$\alpha$ defective-surface plane.

In the case of H$_2$O adsorption there is evidence for a contribution to $\Delta E_{ads}$ from hydrogen bonding between H and surface O atoms. Fig. 4b, shows, as an example, the optimized structure for the Al$_{12}$O$_{48}$ (PHT) cluster which exhibits an H-bond with r(C=O) = 1.964 Å. This complicates somewhat an interpretation of $\Delta E_{ads}$ strictly in terms of dative-bond formation. Nevertheless, the trend in $\Delta E_{ads}$ vs. $\epsilon_S$ is in accord with that expected on the basis of the results for the phosphonyl species.

Another comparison can be made for the adsorption of CO, a weak Lewis base often used to probe the acidity of oxide surfaces. Adsorption occurs (e.g., Ref. [22]) via an Al–C=O dative bond involving the 5$s$ orbital of CO which is the HOMO. A DFT calculation, as described above, was done for the (1 1 1)$\alpha$-oriented 2-DPS using 6-311G(d) basis sets$^1$ for CO and a (1 x 1) surface unit cell with a CO at every surface Al(T$_d$) site. Presumably the same considerations affect similar adsorption processes for other systems. Table 3 and Fig. 5 demonstrate the sensitivity of $\Delta E_{ads}$ to $\epsilon_S$ and $\epsilon_p$. In the absence of experimental data for $\Delta E_{ads}$ it is necessary to compare the cluster results with those for a 2-DPS. Such comparisons for H$_2$O and CO (see above) indicate that the Al$_{12}$O$_{48}$ PHT cluster at the (VWN + PBE)/TZP level gives the most accurate $\Delta E_{ads}$ in comparison to the 2-DPS model of the defective-surface (1 1 1)$\alpha$ surface. Therefore by implication this model, of the three studied here, gives the most reliable representation of S1 for that surface. On the other hand, $\epsilon_s$ for the Al$_{12}$O$_{30}$ PHT cluster is close to that found for the Al(T$_d$) site on the (1 1 0) non-slip surface. Consistent with this, the $\Delta E_{ads}$ values for CO adsorption are also found to be close for these two substrates.

It might appear that issues involved in the formulation of cluster models could be avoided simply by working exclusively with 2-DPS models. However, the molecules of interest here and in other CWA studies are comparable in size to, or larger than, the γ-Al$_2$O$_3$ (1 x 1) surface unit cell. Avoiding significant steric interaction between nearest-neighbor adsorbates in a 2-DPS calculation requires the use of a suitably large slab supercell which may make the calculation computationally intractable. Hence, clusters are still preferable (or even mandatory), provided that $\epsilon_S$ can be reliably obtained. Having constructed such a cluster model one can then proceed with some confidence that reasonable adsorption results will be computed.

It is worthwhile to re-examine previous work [3] in light of the present results. Absolute adsorption energies may be difficult to compute reliably for any model (cluster or 2-DPS) because of the need to reproduce the experimental $\epsilon_S$ which may itself be uncertain, as is the case here. However, other quantities of interest include the adsorption geometry (i.e., lengths and angles of the chemisorption bonds), shifts in adsorbate vibrational frequencies relative to the gas phase and, especially, relative adsorption energies for similar molecules or for different functional groups of the same molecule. These kinds of information can often be obtained even in calculations that are only qualitative with regard to the absolute $\Delta E_{ads}$.

Consider, for example, $\Delta E_{ads}$ for the adsorption of DMMP vs. Sarin (Table 3). The Al$_{12}$O$_{48}$ results are in qualitative agreement with those obtained previously [3] for the much simpler Al$_{21}$O$_{12}$ model which show a larger $\Delta E_{ads}$ for DMMP. However, the difference of 1.6 kcal/mol is less than the previous estimate of

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$^1$ The C and O basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/02/06, developed and distributed by the Molecular Science Computing Facility; Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory; P.O. Box 999; Richland, WA 99352; USA.
8.2 kcal/mol. The difference in $\Delta E_{ads}$ for the two molecules is now understood to result from the somewhat smaller $\varepsilon_H$ of DMMP. Another example concerns adsorption via an Al bond to the phosphonyl vs. the alkoxy O atom of DMMP or Sarin. For Sarin at the B3LYP/6-311G(d) level, the simple Al$_2$O$_3$ cluster gives $\Delta E_{ads} = -30.9$ kcal/mol for bonding to the alkoxy O atom vs. $-49.0$ kcal/mol for bonding to the P=O, a difference of about 18 kcal/mol. A similar difference, $-20.9$ vs. $-39.8$ kcal/mol, is found at the (VWN + PBE)/TZP level for adsorption on the Al$_3$O$_4$$_{36}$ PHT cluster.

When considering the effects of different ligands on the relative adsorption energies of phosphonyl species it should be possible to use the easily-computed $\varepsilon_H$ of the free molecule as a quantitative indicator. In view of the above discussion concerning $\varepsilon_H$ adsorption, such use of $\varepsilon_H$ involves an assumption that other forms of interaction, such as H-bonding, can be neglected. Likewise, in comparing relative adsorption energies for Lewis-acid sites on other oxides, insight can be obtained by computing (or measuring) $\varepsilon_H$. One assumes here that the substrate orbital involved in the adsorption corresponds to a well-defined surface state lying in the band gap and that any modification of the surface does not cause a significant change in the electronic structure of the surface state.

Similar considerations might apply even when the HOMO is not derived from NBOs on the $P$-H group. In this case are derived largely from NBOs on the nitrogen and phosphorus atoms. The calculated values of the adsorption energy for bonding to the phosphonyl group (HOMO-2 and HOMO-3) are computed to be $6.36$ and $6.72$ eV, respectively. Using the average for the phosphonyl group gives $\Delta E_{ads} = -43.4$ kcal/mol for adsorption on Al$_3$O$_4$$_{36}$ PHT cluster. This compares reasonably well with the calculated value [4] of $-39.2$ kcal/mol.

5. Conclusions

Density functional theory has been applied to study the adsorption of a series of phosphonyl compounds on $\gamma$-Al$_2$O$_3$. The adsorption energy $\Delta E_{ads}$ shows a linear dependence on the difference between the one-electron orbital energies of the molecular HOMO ($\varepsilon_H$) and the Al(T$_d$)$_3$ surface state ($\varepsilon_S$). Trends in $\Delta E_{ads}$ for different reagents on a given cluster, and for the same molecule on different clusters, can be understood quantitatively in terms of variations in $\varepsilon_H$ and $\varepsilon_S$.

Cluster models can be constructed which give $\varepsilon_S$ in good agreement with two-dimensionally-periodic slab (2-DPS) predictions based on fundamentally-different models for the $\gamma$-Al$_2$O$_3$ bulk lattice. For test molecules such as H$_2$O and CO, properly-constructed clusters then give $\Delta E_{ads}$ results in good agreement with those from the corresponding 2-DPS calculations. Cluster models can thus be a viable alternative to 2-DPS calculations in the treatment of adsorption on a complex oxide such as $\gamma$-Al$_2$O$_3$.

The results may be extensible to other, non-phosphonyl species. For adsorption of CO via an Al–O bond, $\Delta E_{ads}$ values obtained from 2-DPS calculations agree well with cluster-model predictions based on a linear extrapolation of the phosphonyl results. Thus $\Delta E_{ads}$ for phosphonyls, and perhaps for other species that adsorb by a similar dative-bond formation, can be estimated quantitatively using the easily-computed $\varepsilon_H$ of the free molecule.

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References
