

Sequential addition of H₂O, CH₃OH, and NH₃ to Al₃O₃⁻: A theoretical study

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Photoelectron spectra of two species, Al₃O₃(H₂O)₂⁻ and Al₃O₃(CH₃OH)₂⁻, that are produced by the addition of two water or methanol molecules to Al₃O₃⁻ are interpreted with density-functional geometry optimizations and electron propagator calculations of vertical electron detachment energies. In both cases, there is only one isomer that is responsible for the observed spectral features. A high barrier to the addition of a second molecule may impede the formation of Al₃O₃N₂H₆⁻ clusters in an analogous experiment with NH₃. © 2007 American Institute of Physics. [DOI: 10.1063/1.2409293]

INTRODUCTION

Reactivity at defects in the surfaces of bulk aluminum oxides may be approximated by collisions between Al_xO_y⁻ clusters and molecules of water, methanol, and ammonia. Products of such reactions have been characterized with mass spectrometry and anion photoelectron spectroscopy by Jarrold and co-workers¹⁻³ Experiments on anionic aluminum oxide clusters^{1,4-10} and related theoretical interpretations^{2,3,11-20} indicate that more than one isomer may be represented in photoelectron spectra. The relative abundance of Al₃O₃(H₂O)_n⁻ and Al₃O₃(CH₃OH)_n⁻ species with $n=0, 1, \text{ or } 2$ in mass spectra contrasts with the absence of species with $n \geq 3$. Whereas two well-defined peaks appear in the photoelectron spectra of anions with $n=0$ or 2 , for $n=1$ only overlapping humps are seen. A recent theoretical interpretation of these results²¹ suggests a qualitative difference in bonding between the anions with $n=1$ and $n=0$. Similar methods were employed in a theoretical study²¹ on the addition of an ammonia molecule to Al₃O₃⁻, and the results motivated experimental and additional computational studies on this system.³ These works agree that Al₃O₃NH₃⁻ and Al₃O₄H₂⁻ have similar structures and spectra. However, the latter anion's ability to add a second molecule of water contrasts with the apparent failure of Al₃O₃NH₃⁻ to react with NH₃.³ Wyrwas *et al.*³ ascribed this difference to higher electron density on the reactive, central Al atom (where addition of the second molecule is initiated) that is bound to an NH₂ group in Al₃O₃NH₃⁻ versus its counterpart that is bound to the more electronegative OH ligand in Al₃O₄H₂⁻.

In the photoelectron spectra of species with formulas Al₃O₃(H₂O)_n⁻ and Al₃O₃(CH₃OH)_n⁻, two well-defined peaks appear for $n=0$ and 2 . For ammonia, there is no evidence for

a reaction with a second molecule. The clear differences between the photoelectron spectrum of Al₃O₃⁻ and the spectra of clusters formed with one added molecule of water, methanol, or ammonia have been explained.^{19,21} However, some unanswered questions remain for the products that are formed with two molecules of H₂O, CH₃OH, and NH₃. First, why do the photoelectron spectra of anions formed with two (but not one) molecules of water and methanol resemble the spectrum of Al₃O₃⁻? Second, why does Al₃O₃⁻ react with ammonia to form a cluster with one added NH₃ molecule, but not two? To answer these questions and to gain insights into relationships between electronic structure and reactivity, we report stable structures, relative energies, transition states, and vertical electron detachment energies (VEDEs) for Al₃O₃(H₂O)₂⁻, Al₃O₃(CH₃OH)₂⁻, and Al₃O₃(NH₃)₂⁻.

METHODS

Geometry optimizations without symmetry constraints were performed with the GAUSSIAN 03 program²² in the B3LYP/6-311+G(2d,p) approximation.^{23,24} Previous work indicates that B3LYP/6-311+G(2d,p) optimizations are likely to provide accurate results.¹⁴ To locate transition states, the synchronous, transit-guided, quasi-Newton method²⁵ was used. Optimized minima and transition states were confirmed with harmonic frequency analysis.

B3LYP/6-311+G(2d,p) geometries were assumed in electron propagator²⁶ calculations of the VEDEs with the P3 approximation²⁷ and the 6-311+G(2df,p) basis set,²⁴ except for the clusters involving methanol where only *d* polarization functions were used instead of the *2df* set. For every electron detachment energy calculated with the P3 method, there is a Dyson orbital, φ^{Dyson} , that describes the corresponding change in electronic structure, where

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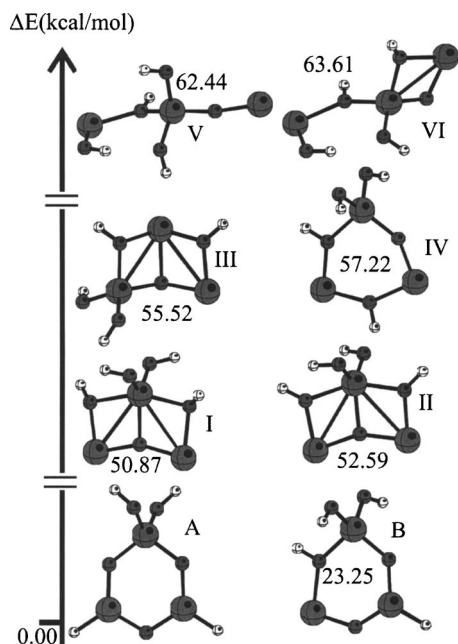


FIG. 1. B3LYP/6-311+G(2d,p) structures and relative energies of $\text{Al}_3\text{O}_5\text{H}_4^-$ isomers.

$$\varphi^{\text{Dyson}}(x_1) = N^{-0.5} \int \psi_{\text{anion}}(x_1, x_2, x_3, \dots, x_N) \psi_{\text{neutral}}^* \times (x_2, x_3, x_4, \dots, x_N) dx_2 dx_3 dx_4 \dots dx_N,$$

x_i is the space-spin coordinate of the i th electron and N is the number of electrons in the anion. The normalization integral of a given Dyson orbital is called the pole strength. Perturbative approximations such as the P3 method work best when pole strengths exceed 0.85. Molecular pictures were generated with BALL & STICK.²⁸

RESULTS AND DISCUSSION

$\text{Al}_3\text{O}_4\text{H}_2^- + \text{H}_2\text{O}$

Figure 1 shows the most stable structures for clusters with the $\text{Al}_3\text{O}_5\text{H}_4^-$ formula. The lowest isomer (A) has C_2 symmetry with two Al–H bonds and two hydroxyl groups. The second lowest structure (B) is 23.25 kcal/mol higher in energy and has just one Al–H bond. In a previous paper,²⁹ high barriers to the cleavage of O–H bonds followed by formation of Al–H bonds were shown to prevent structures with hydride ligands from being formed under the conditions obtained in currently available $\text{Al}_3\text{O}_3(\text{H}_2\text{O})_n$ photoelectron spectra.¹ Therefore, despite the relative stability of isomers with Al–H bonds, we presently consider hydrogen-bonded and dissociative adsorption products (structures I–VI of Fig. 1) for the reaction of $\text{Al}_3\text{O}_4\text{H}_2^-$ and H_2O . Three-body interactions between two water molecules and Al_3O_3^- have been ignored.

We have shown^{21,29} that in the $\text{Al}_3\text{O}_3^- + \text{H}_2\text{O}$ experiment, at least three different $\text{Al}_3\text{O}_4\text{H}_2^-$ isomers can be formed. The energy difference between these three isomers lies in an interval of ~ 2.3 kcal/mol at the MP2/6-311+G(2d,p) level,

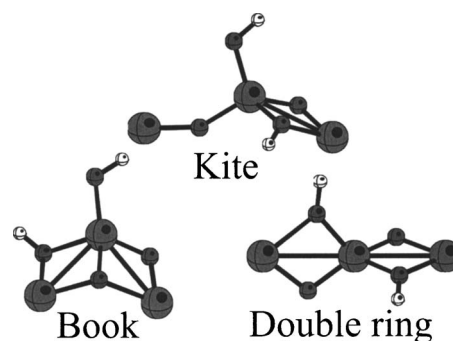


FIG. 2. $\text{Al}_3\text{O}_4\text{H}_2^-$ isomers.

with the $\text{Al}_3\text{O}_4\text{H}_2^-$ book isomer being the most stable.²⁹ Reactions of a second water molecule with each of these three isomers (see Fig. 2) are examined presently.

Figure 3 shows the structures that pertain to reactions of the $\text{Al}_3\text{O}_4\text{H}_2^-$ book isomer. The relative energies refer to the limit of dissociation of the second water molecule. Two types of initial geometries were considered: hydrogen-bonded structures and structures containing an electrostatic interaction between a lone pair of electrons on the water molecule and an Al atom in the cluster. The lowest minimum of the former type displays a hydrogen bond between the water molecule and a lateral oxygen of the book cluster. Only a small basis set superposition error of 0.8 kcal/mol is found. A transition state between this hydrogen-bonded minimum and structure I of Fig. 1 is shown in Fig. 4. The barrier to dissociative adsorption of the second water molecule is 8.65 kcal/mol. Because 12.49 kcal/mol is released in the formation of the hydrogen-bonded minimum, structure I is likely to be formed under typical experimental conditions. Structures II–IV also could be relevant to the reaction between the $\text{Al}_3\text{O}_4\text{H}_2^-$ book isomer and H_2O . Structure II is just a rotational isomer of I. Previous calculations^{14,19,21} have es-

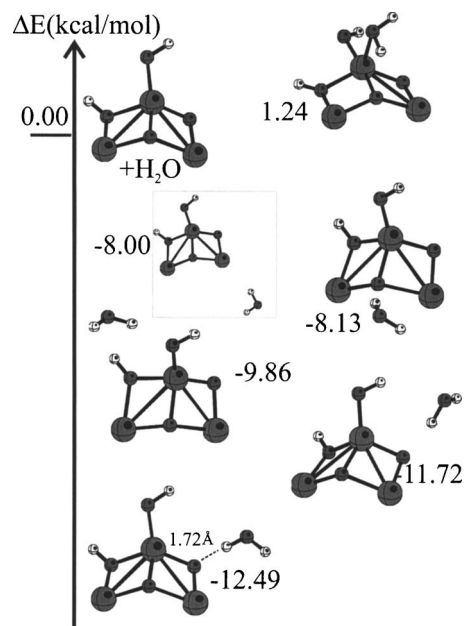


FIG. 3. B3LYP/6-311+G(2d,p) structures and relative energies of book $\text{Al}_3\text{O}_4\text{H}_2^- + \text{H}_2\text{O}$ adsorption products.

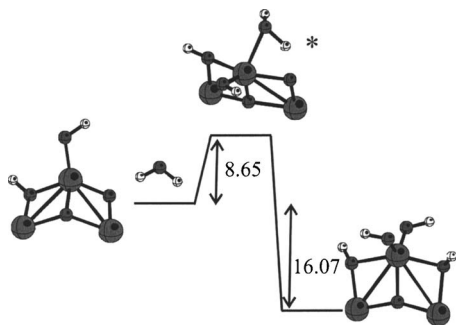


FIG. 4. B3LYP/6-311+G(2d,p) structures and relative energies (kcal/mol) of the book $\text{Al}_3\text{O}_4\text{H}_4^- + \text{H}_2\text{O}$ adsorption product, isomer I, and the transition state that lies between them.

tablished the presence of valence electron pairs on the non-central Al nuclei and therefore interactions between these centers and lone pairs on the water molecule lead to repulsive interactions. Barriers between hydrogen-bonded minima and structure III are likely to be relatively high. Structure IV may be considered to be the product of a similar reaction where the water molecule's proton is transferred to the central, instead of the lateral, oxygen of the book cluster. Proton transfer to the lateral O is expected to be preferred because of the more negative charges on the lateral oxygen.²¹

For the $\text{Al}_3\text{O}_4\text{H}_2^-$ kite and double ring isomers, the lowest adsorption products with a water molecule are hydrogen-bonded structures with formation energies of -12.33 (C) and -11.27 (D) kcal/mol, respectively (Fig. 5). The optimization of the kite isomer interacting with a water molecule through the O atom of the kite's tail leads to the double ring (D) structure.

These initial complexes are related to isomers V and VI of Fig. 1 through proton donation to a bridge oxygen, coordination of an OH group to an Al center, and the migration of an OH group away from a bridging position. Higher barriers may be expected for these relatively complicated reactions, but they cannot be dismissed *a priori*. Therefore, contributions from isomers V and VI to the photoelectron spectra of $\text{Al}_3\text{O}_5\text{H}_4^-$ are considered below.

Table I shows the total formation energies for isomers I, V, and VI, the most probable dissociative adsorption products, respectively, of the reactions between the book, kite, and double ring isomers of $\text{Al}_3\text{O}_4\text{H}_2^-$ and H_2O . The most exothermic reaction produces isomer I from the $\text{Al}_3\text{O}_4\text{H}_2^-$ book structure. Whereas the reagents that form isomers I, V, and VI lie within 3 kcal/mol of each other,²⁹ differences in reaction energies chiefly reflect the relative stability of the

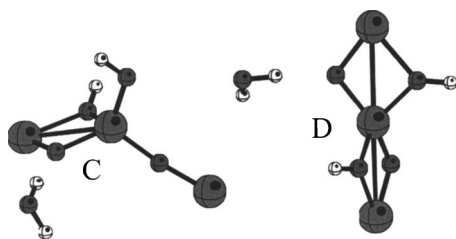


FIG. 5. B3LYP/6-311+G(2d,p) structures of the lowest adsorption products of kite and double ring isomers of $\text{Al}_3\text{O}_4\text{H}_2^- + \text{H}_2\text{O}$.

TABLE I. B3LYP/6-311+G(2d,p) formation energies (kcal/mol).

Reaction	Product (isomer identification number)	Formation energies (kcal/mol)
$\text{Al}_3\text{O}_4\text{H}_2^-$ book + H_2O	I	-28.55
$\text{Al}_3\text{O}_4\text{H}_2^-$ kite + H_2O	V	-17.59
$\text{Al}_3\text{O}_4\text{H}_2^-$ double ring + H_2O	VI	-16.28
$\text{Al}_3\text{O}_4\text{CH}_4^-$ book + CH_3OH	F	-28.50
$\text{Al}_3\text{O}_4\text{CH}_4^-$ kite + CH_3OH	G	-16.78
$\text{Al}_3\text{O}_4\text{CH}_4^-$ double ring + CH_3OH	H	-15.49

products. Table II reports VEDEs for all clusters that remain relevant at this point. The most stable structure of Fig. 1 (A) cannot be responsible for the features observed in the photoelectron spectra, since the calculated VEDEs for this isomer are higher than the experimental ones¹ by several eV. The VEDEs of structure I match quite well with the experimental values of 3.3 and 3.8 eV.¹ The two lowest VEDEs correspond to Dyson orbitals which consist chiefly of antibonding or bonding combinations of Al 3s functions on the lateral aluminum atoms. Structure III can be discarded from further consideration because no signal below 2.5 eV is observed. The photoelectron spectrum alone cannot confirm or disprove the absence or presence of the other isomers.

On the basis of the VEDE predictions and the relative energies, one may conclude that structure I is chiefly responsible for the features of the photoelectron spectrum of $\text{Al}_3\text{O}_5\text{H}_4^-$. Structures IV, V, and VI have VEDEs that may be in plausible agreement with this spectrum, but their relative energies are too high to be present under the corresponding experimental conditions. The antecedent C and D structures are even less stable and therefore may be discarded.

Can structure I react with a third water molecule to produce a stable cluster with the formula $\text{Al}_3\text{O}_3(\text{H}_2\text{O})_3^-$? The experimental mass spectrum does not show a corresponding signal,¹ but B3LYP/6-311+G(2d,p) optimizations produce a hydrogen-bonded structure between the water molecule and one hydroxyl group of the central Al atom of structure I whose energy is 11.63 kcal/mol lower than the dissociation limit of structure I plus a water molecule. This value is similar, respectively, to the formation energies of isomers C and D with respect to kite and double ring $\text{Al}_3\text{O}_4\text{H}_2^- + \text{H}_2\text{O}$. However, the dissociative adsorption of this third water molecule is not expected. The activation of the O-H bond should not occur because it involves a sterically impeded interaction between the water's O and the central Al. Despite the thermodynamic stability of hydrogen-bonded structures, there is little evidence for them in the photoelectron and mass spectra.

The similarity between Al_3O_3^- and $\text{Al}_3\text{O}_5\text{H}_4^-$ photoelectron spectra (and their evident disparities with the spectrum of $\text{Al}_3\text{O}_4\text{H}_2^-$) can be attributed to the equivalence of corner Al atoms in the lowest isomers of these two anions, but of even greater importance is the presence of only one isomer in both cases. This is not the case for $\text{Al}_3\text{O}_4\text{H}_2^-$, where at least three isomers may contribute to the broadening of the spectra.

TABLE II. Vertical electron detachment energies (eV) from Koopmans's theorem (KT) and P3 approximations with the 6-311+G(2*df*,*p*) basis set. For structures containing methoxy groups, the 6-311+G** basis set was used.

Isomer	KT	P3
A	7.60	6.21
	7.84	6.52
	7.91	6.59
	8.20	6.88
I	3.33	3.22
	3.71	3.60
	8.41	6.90
	9.04	7.56
III	2.49	2.33
	3.76	3.63
	9.07	7.54
	9.33	7.80
IV	3.14	3.02
	4.27	4.17
	8.32	6.87
	8.68	7.11
V	3.13	3.07
	5.55	5.58
	8.63	7.13
	8.90	7.37
VI	3.42	3.36
	3.89	3.83
	8.61	7.25
	8.79	7.31
C	3.35	3.28
	5.37	5.41
	8.18	6.71
	8.79	7.24
D	3.67	3.59
	3.90	3.85
	8.44	7.07
	8.92	7.46
F	3.38	3.15
	3.76	3.54
	7.51	5.83
	7.88	6.25
G	3.19	3.02
	5.61	5.54
	7.83	6.16
	8.19	6.52
H	3.49	3.32
	3.92	3.74
	8.47	6.81
	8.67	7.00

$\text{Al}_3\text{O}_4\text{CH}_4^- + \text{CH}_3\text{OH}$

The photoelectron spectrum of $\text{Al}_3\text{O}_5\text{C}_2\text{H}_8^-$ is very similar to that of $\text{Al}_3\text{O}_5\text{H}_4^-$. In a previous work, we found that Al_3O_3^- reacts similarly with water and methanol²¹ and therefore proposed an initial, H-bonded adsorption structure for

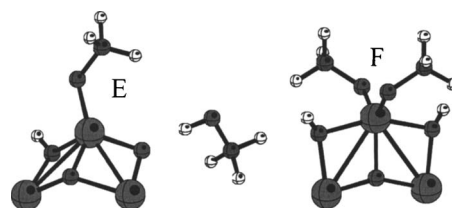


FIG. 6. B3LYP/6-311+G(2*d*,*p*) structures of $\text{Al}_3\text{O}_4\text{CH}_4^-$ book+ CH_3OH adsorption (E) and dissociative adsorption (F) products.

methanol similar to that found with water. The optimized minimum (isomer E of Fig. 6) is 13.03 kcal/mol lower than the separated, $\text{Al}_3\text{O}_4\text{CH}_4^- + \text{CH}_3\text{OH}$ limit. Dissociative adsorption produces isomer F, which is likely to be chiefly responsible for the signals observed in the $\text{Al}_3\text{O}_5\text{C}_2\text{H}_8^-$ photoelectron spectrum and which retains the familiar book structure of isomer I of $\text{Al}_3\text{O}_5\text{H}_4^-$. The formation energy of isomer F, -28.50 kcal/mol (see Table I), is similar to the formation energy of isomer I of $\text{Al}_3\text{O}_5\text{H}_4^-$. We also examined the kite (G) and double ring (H) dissociative adsorption isomers for the $\text{Al}_3\text{O}_4\text{CH}_4^-(\text{CH}_3\text{OH})$ cluster. (See Fig. 7 for the relative energies of the F, G, and H structures.) The initial H-bonded adsorption energies are -13.15 and -12.02 kcal/mol, respectively. The B3LYP formation energies are listed in Table I. The similarity between these results

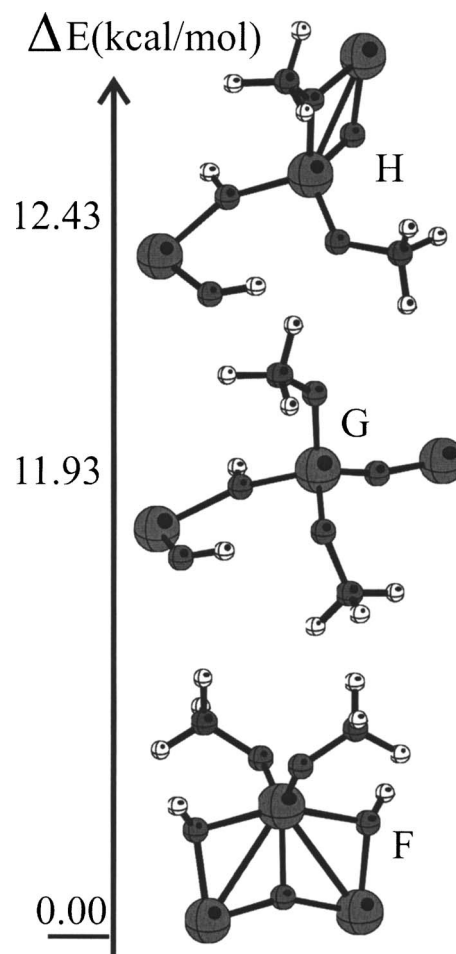


FIG. 7. B3LYP/6-311+G(2*d*,*p*) structures and relative energies of book (F), kite (G), and double ring (H) structures of $\text{Al}_3\text{O}_5\text{C}_2\text{H}_8^-$.

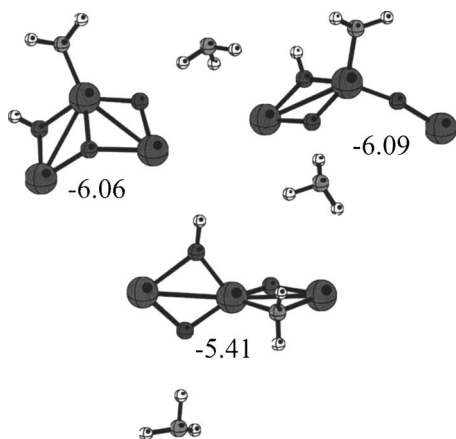


FIG. 8. B3LYP/6-311+G(2d,p) structures and relative energies (kcal/mol) for the first approach of an NH₃ molecule to the book, kite, and double ring forms of Al₃O₃NH₃⁻.

and the ones obtained for the addition of water leads us to the conclusion that the book isomer (F) is the one which is chiefly responsible for the signals of the Al₃O₃C₂H₈⁻ photoelectron spectrum. The calculated VEDEs for structures F, G, and H are shown in Table II. The energy separation between the two lowest VEDEs of the F isomer is in good agreement with the spectrum reported by Akin and Jarrold.¹ As in the case of Al₃O₅H₄⁻, Koopmans results are in better agreement with experimentally derived VEDEs than the P3 predictions.

Al₃O₃NH₃⁻+NH₃

For the reaction between Al₃O₃⁻ and NH₃, the corresponding mass spectrum³ does not indicate the presence of Al₃O₃N₂H₆⁻. Figure 8 shows optimized complexes of NH₃ with the book, kite, and double ring structures of Al₃O₃NH₃⁻ and their corresponding energies with respect to infinite separation. The latter values are less exothermic than their water and methanol counterparts.

Figure 9 shows the reaction energy and the energy barrier for the dissociative adsorption product with the book structure. The latter figure [which is likely to be underestimated by B3LYP (Ref. 30)] exceeds the formation energies of Fig. 8 and could account for the absence of an Al₃O₃N₂H₆⁻ signal in the mass spectrum. The kite and double ring

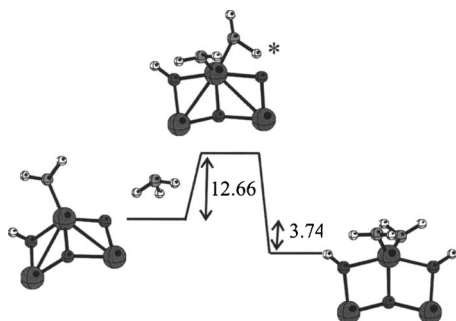


FIG. 9. B3LYP/6-311+G(2d,p) optimized structures and relative energies (kcal/mol) of the lowest book Al₃O₃NH₃⁻+NH₃ adsorption product, the Al₃O₃N₂H₆⁻ book isomer, and the transition state that lies between them.

Al₃O₃N₂H₆⁻ dissociative adsorption products are even less stable, with formation energies with respect to Al₃O₃NH₃⁻+NH₃ of -1.58 and -0.81 kcal/mol, respectively. In these cases, the hydrogen-bonded complexes are more stable.

CONCLUSIONS

Al₃O₃⁻ and the products of its reactions with two molecules of water or methanol have similar photoelectron spectra for two reasons. First, each anion has a favored structure that is kinetically accessible (but not necessarily the most thermodynamically stable) and it is not necessary to invoke less stable isomers in calculating accurate vertical electron detachment energies that account for the spectra. Second, the equivalence of two corner Al atoms in these favored structures produces Dyson orbitals for the two lowest vertical electron detachment energies that consist chiefly of in-phase and out-of-phase combinations of 3s Al atomic orbitals. When only one molecule of water or methanol is dissociatively adsorbed, such equivalence is lost and there may be more than one isomer that is present in the samples that are prepared by current experimental techniques. Whereas one molecule of NH₃ is adsorbed dissociatively with Al₃O₃⁻ to produce an anion with OH and NH₂ ligands that are coordinated to Al centers, only a hydrogen-bonded complex between the latter anion and a second ammonia molecule has been found. Because the energy barrier between this complex and a product with two OH and two NH₂ groups exceeds the initial coordination energy, the latter species might not be observed in the Al₃O₃⁻+NH₃ experiment. These conclusions are supported by geometry optimizations and relative energies on anion species and by corresponding electron propagator calculations of vertical electron detachment energies.

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