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1.0 Summary

The AM1 semiempirical quantum chemical method was used to model the interaction of perfluoroethers with aluminum surfaces. Perfluorodimethoxymethane and perfluorodimethyl ether were studied interacting with aluminum surfaces, which were modeled by a five-atom cluster and a nine-atom cluster. Interactions were studied for edge (high index) sites and top (low index) sites of the clusters. Both dissociative binding and nondissociative binding were found, with dissociative binding being stronger. The two different ethers bound and dissociated on the clusters in different ways: perfluorodimethoxymethane through its oxygen atoms, but perfluorodimethyl ether through its fluorine atoms. The acetal linkage of perfluorodimethoxymethane was the key structural feature of this molecule in its binding and dissociation on the aluminum surface models. The high-index sites of the clusters caused the dissociation of both ethers. These results are consistent with the experimental observation that perfluorinated ethers decompose in contact with sputtered aluminum surfaces.

2.0 Introduction

The long-term stability of perfluorinated ethers (PFE's) in contact with metals or metal oxides is of technological interest because of their current and future use in space mechanisms (ref. 1), computer disk drives (ref. 2), and, potentially, in advanced gas turbine engines (ref. 3). A literature survey of this research area revealed over 50 publications in the last 6 years. Most of these are experimental studies of the products of catalyzed lubricant decomposition after thermal or mechanical stress and attempts to deduce a chemically reasonable decomposition mechanism from the data (refs. 4 to 7). One factor that has emerged as important to perfluoroalkyl ether stability in real tribological systems is the presence in the ether chain of the acetal linkage ($–OCF_2O–$) (refs. 6 to 10). Numerous experimental studies have shown that acetal-containing fluoroethers are more vulnerable to catalyzed breakdown in the presence of metal (ref. 6) or metal oxide (refs. 9 and 10) surfaces. Herrera-Fierro et al. (ref. 6) performed experimental studies in 1992 which showed that a freshly sputtered aluminum surface caused room-temperature decomposition of acetal-containing lubricant molecules; gold surfaces and, importantly, sputtered 440 °C steel surfaces were unreactive below 190 °C. In a subsequent x-ray photoelectron spectroscopy (XPS) study John and Liang (ref. 11) detected no interaction between any of several simple fluoroethers and clean polycrystalline aluminum or iron surfaces.

The relative reactivity of aluminum versus iron surfaces has important consequences for the design of real tribological systems. Of interest also is the role of the acetal group in the catalyzed breakdown. Researchers have different views as to the importance of surface Lewis-acid sites in the decomposition. Kasai, Tang, and Wheeler (ref. 10) have proposed a mechanism for decomposition on aluminum oxide (Al_2O_3) surfaces involving Lewis-acid attack at the ether oxygen atoms. However, Ng et al. (ref. 12) have performed transmission infrared spectroscopy experiments of simple fluoroethers on powdered Al_2O_3 which suggest that Lewis-acid sites are not involved in the decomposition. Additionally, HREELS and TDS experiments (ref. 13) on Al_2O_3 single crystals with adsorbed partially fluorinated dimethyl ethers have shown that Al_2O_3 is unreactive to $(CH_3)_2O$ or $(CF_2H)_2O$.

A quantum chemical modeling study was undertaken to further understanding of how and why perfluorinated ethers break down on some surfaces but not on others. The interactions of two simple perfluoroethers with five-atom and nine-atom aluminum clusters were investigated.

3.0 Methods

To keep the calculations tractable, reasonably sized models were chosen for PFE's and for the metal surface. The lubricant was modeled by two simple PFE's: (1) perfluorodimethoxymethane (PFDMM), $CF_3–O–CF_2–O–CF_3$, containing an

acetal linkage, and (2) perfluorodimethyl ether (PFDM), CF_3–O–CF_3. Cluster models were used to represent the aluminum surface. Two surface models were used: a five-atom cluster and a nine-atom cluster. These model surfaces were constructed from the coordinates of the (100) face of a bulk α-aluminum crystal (ref. 14). The five-atom cluster consisted of a single layer of aluminum atoms (fig. 1), and the nine-atom cluster contained four more aluminum atoms as a second layer beneath the hollows of the top layer. Two possible interaction sites were examined on each of the metal clusters: (1) a top site, represented by the middle atom of the five-atom layer, and (2) an edge site, represented by an edge atom.

Because of the relatively large system being studied, semiempirical methods were used. The semiempirical molecular orbital package used was MOPAC 93 (ref. 15). AM1 (ref. 16) was selected as the most suitable semiempirical method, on the basis of benchmarking studies in which AM1 and MNDO results were compared with ab initio calculations for PFDMM alone, for PFDM alone, and for an Al+ ion interacting with both ethers. In these benchmarking calculations PFDM was studied at the HF/6–31G* and MP2/6–31G*//HF/6–31G* levels of theory, and PFDMM was studied at the HF/3–21G level. All results reported herein are based on calculations in which the cluster was fixed in its bulk geometry and the ether was fully optimized (unless otherwise noted). The eigenvector-following routine (ref. 17) implemented in MOPAC 93 was used for all geometry optimizations. The spin states of the Al_5 and Al_9 clusters, as well as those of all ether/cluster complexes, were assumed to be doublets. The MECI method (ref. 18) was used for these open-shell systems.

4.0 Results and Discussion

An initial comparison of using AM1 versus MNDO for this modeling study was done by calculating the interaction energy of PFDMM with the five-atom aluminum cluster. Without experimental measurements or ab initio calculations, the most important factor to examine is the binding energy of the complex. The binding energy is defined as the difference between the energy of the complex and the sum of the energies of the ether alone and the cluster alone. For a system to be considered bound, the energy of the complex must be lower than the sum of the components. Table I shows the results of these calculations. AM1 gave a larger binding energy and, in agreement with the benchmarking, was chosen as the more suitable method.

The results for each ether interacting with the aluminum clusters will be discussed separately. For each ether, the discussion is divided into two parts: (1) the interaction of the ether at an edge site and (2) the interaction of the ether at the top site. Within each of these subsections, results for the five-atom cluster and the nine-atom cluster are discussed in turn.

4.1 Perfluorodimethoxymethane

Initial optimizations of PFDMM interacting with either the edge site or the top site of the five-atom aluminum cluster showed that the ether was strongly bound when its oxygen atoms were oriented toward the cluster. Hence, all calculations of PFDMM interacting with the aluminum clusters started with the optimized structure of the ether and with the ether's oxygen atoms pointing toward the cluster.

4.1.1 Edge Site

Five-atom cluster.—The initial geometry optimization of PFDMM interacting with an edge site of the five-atom aluminum cluster (fig. 1) revealed a system bound by 3.80 eV with dissociation of the ether. This dissociation was indicated by an increase in one carbon-oxygen (C(6)–O(8)) reaction coordinate from 1.46 to 2.85 Å, well beyond the carbon-oxygen covalent bond length. These encouraging results prompted further investigation of this interaction.

To better characterize the decomposition process, a reaction coordinate was defined as the distance between the ether's central carbon atom and one of the edge aluminum atoms. By fixing this parameter and allowing the ether to relax (optimize), the decomposition was found to occur over the range 2.50 to 2.60 Å. Table II and figures 2 to 5 show the results of these calculations. Electrostatic interactions appeared to play a key role in the interaction between the ether and the cluster (table II).

TABLE I.—COMPARISON OF METHODS (MNDO VS AM1) FOR EXAMINING INTERACTION OF FIVE-ATOM Al CLUSTER AND PERFLUORODIMETHOXYMETHANE

Molecule	MNDO	AM1
	Interaction energy, eV	
PFDMM	–4866.35	–4910.09
Five-atom cluster	–226.94	–238.80
PFDMM/cluster complex	–5093.70	[a]–5152.69
Binding energy, eV	0.41	3.80

[a]See figure 1.

TABLE II.— RESULTS OF CALCULATIONS EXAMINING MOVEMENT OF PERFLUORODIMETHOXYMETHANE TOWARD FIVE-ATOM Al CLUSTER
[See figures 2 to 5.]

Reaction coordinate, Å		Binding energy, eV	Charge for Al(2)	Charge for O(8)
C(6)–Al(2)	C(6)–O(8)			
2.60	1.41	0.05	0.43	–0.32
2.57	1.48	0.44	0.52	–0.25
2.55	1.48	0.42	0.52	–0.25
2.53	2.91	2.30	0.60	–0.51
2.50	2.75	3.76	0.56	–0.50

As the distance between the ether and the cluster decreased, the edge aluminum atom became more positive and the ether oxygen atoms became more negative. This interaction was not purely electrostatic; significant orbital overlap existed between the edge aluminum atom and the ether's oxygen atoms (*vide infra*).

Nine-atom cluster.—To improve the surface model, the interaction of this ether with the edge site of the nine-atom cluster was investigated. For this system, two different types of binding were found: nondissociative binding, with a binding energy of 1.85 eV (fig. 6); and dissociative binding, found by reorienting the ether relative to the cluster and reoptimizing the ether, with a binding energy of 3.62 eV (fig. 7). This dissociative state on the edge site of the nine-atom cluster was similar to that found for the edge site of the five-atom cluster (table III).

4.1.2 Top Site

Five-atom cluster.—Interaction between PFDMM and the top site of the five-atom cluster showed both nondissociative and dissociative binding (figs. 8 and 9). The nondissociative binding state was a complex bound by 2.00 eV. The dissociative binding state had a binding energy of 4.69 eV, and one of the ether C–O reaction coordinates increased to 4.54 Å from its initial value of 1.40 Å. Although these optimizations were started with the ether positioned above the cluster's top site, the dissociated fragments were bound to *edge* aluminum atoms (fig. 9). For both dissociative and nondissociative binding at the top site, the interaction between the fluorine atoms and the edge aluminum atoms was more pronounced than the interaction calculated for the edge site.

Nine-atom cluster.—The interaction between PFDMM and the top site of the nine-atom aluminum cluster was also studied. Again, both nondissociative and dissociative binding were found (figs. 10 and 11), but with a smaller difference in binding energy (table IV) than in the previously discussed results. Again, although the optimization was started with the ether at the top site, dissociative binding occurred instead with the edge atoms.

TABLE III.— RESULTS FOR FIVE-ATOM AND NINE-ATOM PERFLUORODIMETHOXYMETHANE DISSOCIATED COMPLEXES
[Edge site; see figures 1 and 7, respectively.]

	PFDMM/five-atom complex	PFDMM/nine-atom complex
	Reaction coordinate, Å	
C(6)–Al(2)	2.42	2.40
C(6)–O(7)	1.46	1.46
C(6)–O(7)	2.85	2.95
Binding energy, eV	3.80	3.62

TABLE IV.—NONDISSOCIATIVE AND DISSOCIATIVE BINDING ENERGIES OF PERFLUORODIMETHOXYMETHANE ON FIVE-ATOM AND NINE-ATOM Al CLUSTERS

Complex	Nondissociative binding energy, eV	Dissociative binding energy, eV
Five-atom cluster/PFDMM (top site)	[a]1.99	[b]4.69
Nine-atom cluster/PFDMM (edge site)	[c]1.85	[d]3.62
Nine-atom cluster/PFDMM (top site)	[e]3.33	[f]3.62

[a]See figure 8.
[b]See figure 9.
[c]See figure 6.
[d]See figure 7.
[e]See figure 10.
[f]See figure 11.

4.2 Perfluorodimethyl Ether

Initial optimizations of PFDM interacting with the edge and top sites of the five-atom aluminum cluster showed that the ether bound much more strongly when its oxygen atoms were oriented away from the cluster. Calculations of PFDM interacting with the aluminum clusters are reported here in the following order: first, with the ether's oxygen atoms pointing away from the cluster; then, with the atoms oriented toward the cluster. In all cases, the ether's initial geometry was that found in the first optimization reported as follows.

4.2.1 Interaction Through Fluorine Atoms

Edge site.—The initial geometry optimization of PFDM interacting at an edge site of the five-atom cluster revealed a system bound by 2.71 eV with no dissociation of the ether (fig. 12). Both C–O reaction coordinates were 1.39 Å. Dissociative binding was also found for PFDM interacting at the edge site with a binding energy of 6.10 eV (fig. 13). The C(8)–O(6) bond reaction coordinate was 4.14 Å, indicating a broken C–O bond. The C(7)–O(6) bond reaction coordinate was 1.29 Å, indicating C=O bond character. The prevalent binding mode appeared to be fluorine atom interactions with the aluminum cluster. Table V summarizes these results.

For PFDM interacting with an edge site on the nine-atom cluster, dissociative binding was found, similar to that found for the five-atom cluster (fig. 14). In addition, the perturbed ether's bond lengths and angles were comparable to those resulting from interaction with the five-atom cluster, and its orientation was only slightly different from that of the dissociatively bound PFDM on the five-atom cluster.

Top site.—An initial geometry optimization revealed a system bound by 2.83 eV (fig. 15). The reaction coordinates were

TABLE V.—PERFLUORODIMETHYL ETHER EDGE-SITE INTERACTIONS WITH FIVE-ATOM Al CLUSTER: COMPARISON OF NONDISSOCIATIVE AND DISSOCIATIVE BINDING

Binding	Reaction coordinate, Å			Binding energy, eV
	C(7)–O(6)	C(8)–O(6)	Al(2)–O(6)	
Nondissociative[a]	1.39	1.39	3.15	2.71
Dissociative[b]	1.29	4.14	2.43	6.10

[a]See figure 12.
[b]See figure 13.

TABLE VI.—PERFLUORODIMETHYL ETHER TOP-SITE INTERACTIONS WITH FIVE-ATOM AND NINE-ATOM Al CLUSTERS

Cluster	Reaction coordinate, Å				Binding energy, eV
	Al(1)–O(6)	C(7)–O(6)	C(8)–O(6)	C(8)–F(13)	
Five atom[a]	4.31	1.37	1.39	4.70	8.26
Nine atom[b]	4.30	1.36	1.39	4.84	7.26

[a]See figure 17.
[b]Not pictured.

TABLE VII.—PERFLUORODIMETHYL ETHER INTERACTIONS WITH FIVE-ATOM Al CLUSTER: O ATOM DIRECTED TOWARD SURFACE

Site	Reaction coordinate, Å				Binding energy, eV
	Al(2)–O(6)	Al(1)–O(6)	C(7)–O(6)	C(8)–O(6)	
Edge[a]	2.22	– – – – – –	1.41	1.42	0
Top[b]	– – – – – –	2.50	1.42	1.41	0.09

[a]See figure 18.
[b]See figure 19.

1.38 and 1.39 Å for the C(7)–O(6) and C(8)–O(6) bonds, respectively. Fluorine-aluminum interactions were again the prevalent mode of binding. Another bound ether-cluster complex was found when the ether was optimized at the initially closer Al(1)–O(6) reaction coordinate of 2.50 Å (fig. 16), which was fixed. This system was bound by 7.90 eV. The reaction coordinates were 1.40 and 1.38 Å for the C(8)–O(6) the C(7)–O(6) bonds, respectively. One of the fluorine atoms was pulled off the ether and onto the cluster. A full optimization of this system (including the aluminum-oxygen distance) gave a similar result, with a slightly larger binding energy of 8.26 eV (fig. 17). Although a C–F bond was broken in this case, the C–O–C linkage of the ether remained intact. As for PFDMM, when PFDM was optimized starting above the top site, dissociative binding occurred through interaction with edge aluminum atoms.

The interaction of PFDM with the top site of the nine-atom cluster was also examined. Table VI compares the results for PFDM interacting with both the five-atom and nine-atom clusters. As for PFDMM, the interaction of PFDM with the nine-atom cluster was comparable to that with the five-atom cluster.

4.2.2 Interaction Through Oxygen Atoms

In the results presented thus far for PFDM the initial orientation chosen had the oxygen atoms directed away from the aluminum clusters. Studies were also performed with the PFDM oxygen atoms directed toward the clusters, for both the edge site and the top site of the five-atom cluster. Table VII gives the results of this study. For both the edge site and the top site no dissociation was observed and minimal or no binding occurred between the ether and the cluster (figs. 18 and 19).

The reason that PFDMM binds to the aluminum surface models through its oxygen atoms but PFDM does not can be found in the electronic structures of ether-cluster complexes. Figure 20 compares the orbital energy levels of the Al_5 cluster, the PFDMM/Al_5 complex, and the PFDM/Al_5 complex with both ethers interacting with an edge site of the cluster. The cluster orbital energies were more stabilized for the PFDMM/Al_5 system than for the PFDM/Al_5 system when the ethers were both about 1.8 Å from the cluster, the optimal reaction coordinate for PFDMM. For PFDM, the corresponding optimal reaction coordinate was 2.50 Å because a closer approach destabilized the cluster energy levels. Figure 20 also depicts the

orbital interaction of PFDMM that most stabilized the cluster. The next lower orbital interaction, also quite stabilized, is similar in appearance. The symmetry of PFDMM caused its strong orbital interactions with an aluminum atom on the surface model. Much orbital overlap was possible because two oxygen atoms bonded to the aluminum atom. Overlap was not possible for PFDM because it has only one oxygen atom.

5.0 Conclusions

Even though simple models of perfluoroether lubricants and aluminum surfaces were used here, the extensive geometry optimizations performed made it necessary to use a semiempirical quantum chemical method rather than an ab initio one. Although the approximate nature of semiempirical results must be stressed, such methods are reliable for predicting trends. An example from the present work of such a trend is the stronger binding energies always observed when the ethers dissociated on the clusters, as compared with the nondissociative binding energies. Another important proviso in interpreting the present results is the inherent multiple-minimums problem. Although several starting points were investigated for the interaction of each ether with each cluster site, there are many local minimums in such a system and no attempt was made to ensure that global minimums were found.

Both dissociative and nondissociative binding were found for the interactions of PFDMM and PFDM with the five-atom and nine-atom aluminum surface models. A key finding from this work is that dissociative binding was stronger than nondissociative binding for these systems. Hence, dissociation of perfluoroethers on pure aluminum surfaces is the thermodynamically preferred binding mode. However, different types of perfluoroether bind and dissociate differently. For PFDMM, an ether linkage was always broken through oxygen-aluminum bond formation. Dissociation of the ether linkage also occurred for PFDM, but through interactions between its fluorine atoms and the cluster aluminum atoms. For PFDMM, the acetal linkage acted as a Lewis base, which led to its decomposition. In the small cluster models used here, the edge aluminum atoms were partially positively charged and could act as Lewis-acid sites. These findings show the importance of Lewis-acid/base chemistry in the *initial* encounter of a perfluoroether with an aluminum surface. Electronic effects played an important role in the different binding and dissociation modes of PFDMM and PFDM on the aluminum surface models studied here. The orbitals of PFDMM, with its acetal linkage, had the right symmetry to allow much positive orbital overlap with the surface. This was not the case for PFDM.

When either ether was optimized initially on a top site, dissociative binding was observed only through interactions with edge aluminum atoms. This result agrees with the experimental observation that perfluorinated ether lubricants readily break down on sputtered aluminum surfaces but not on annealed aluminum surfaces.

For both perfluoroethers, both the five-atom and nine-atom clusters generally gave comparable results in terms of energies and final orientation. Therefore, the inclusion of a second layer may not be necessary for studying these interactions. Even though the second layer was an attempt to improve the surface model, a more extensive one-layer surface model might be a better use of computer resources.

The present results on the interactions of perfluoroethers with cluster models of aluminum surfaces are encouraging for future semiempirical studies of these systems. A number of possibilities exist for improving the models. Extending the cluster top layer and using a larger ether to better model a commercial lubricant would allow more exploration of dependence on model size. Including d orbitals in the aluminum atoms' electronic structure should also be investigated; the AM1 method used here puts only s and p orbitals on the aluminum atoms. As with all quantum chemical methods, however, size is a limitation in extending the model.

Another possibility is to model the interaction of a fluorinated ether with a different metal surface. Gold may be the best candidate for such studies, since Fomblin Z has been found to be unreactive on gold. Other surfaces, such as aluminum oxide or iron, are also of interest.

Acknowledgments

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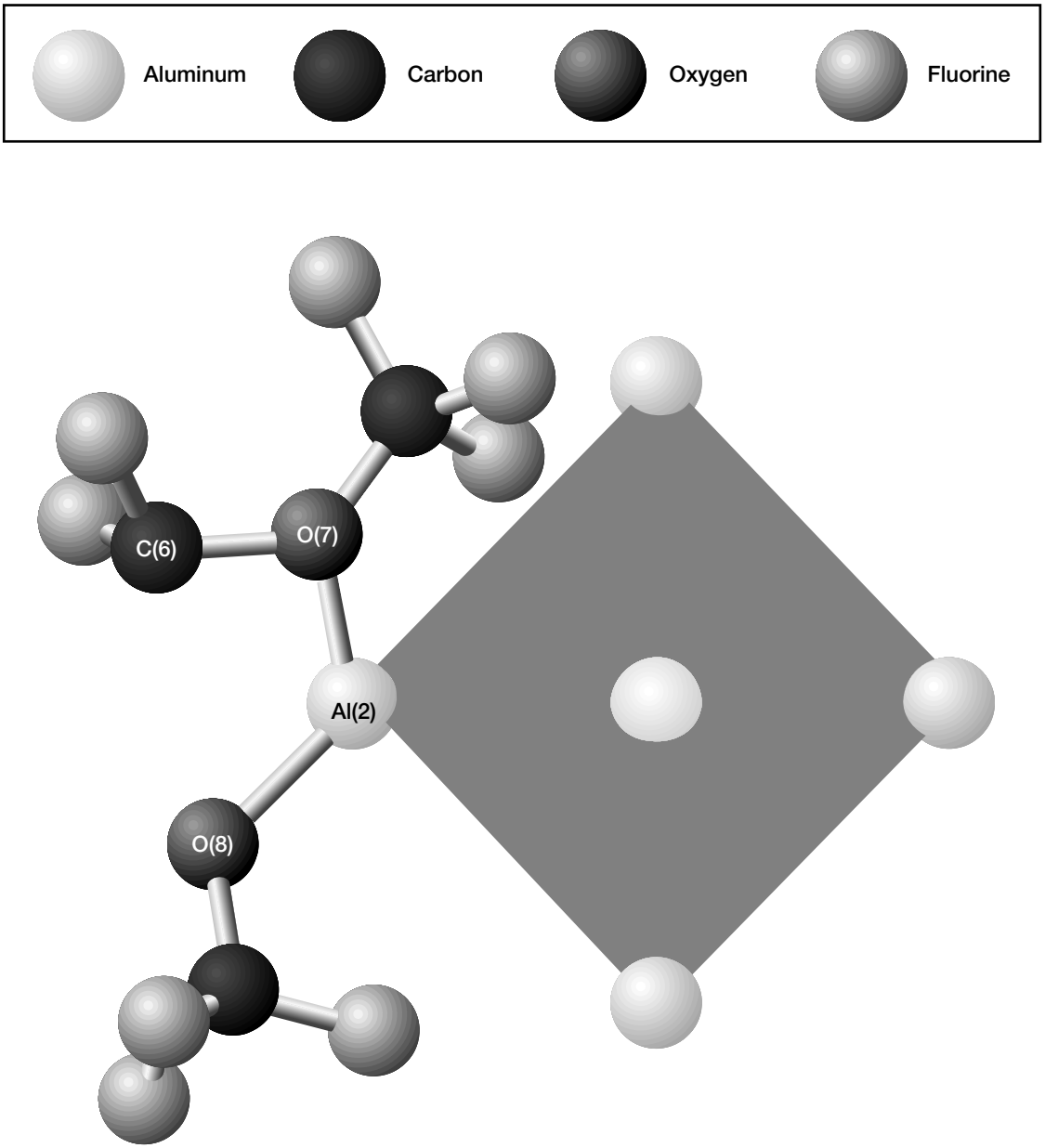

Figure 1.—Five-atom Al cluster/dissociated perfluorodimethoxymethane complex: edge site (AM1).

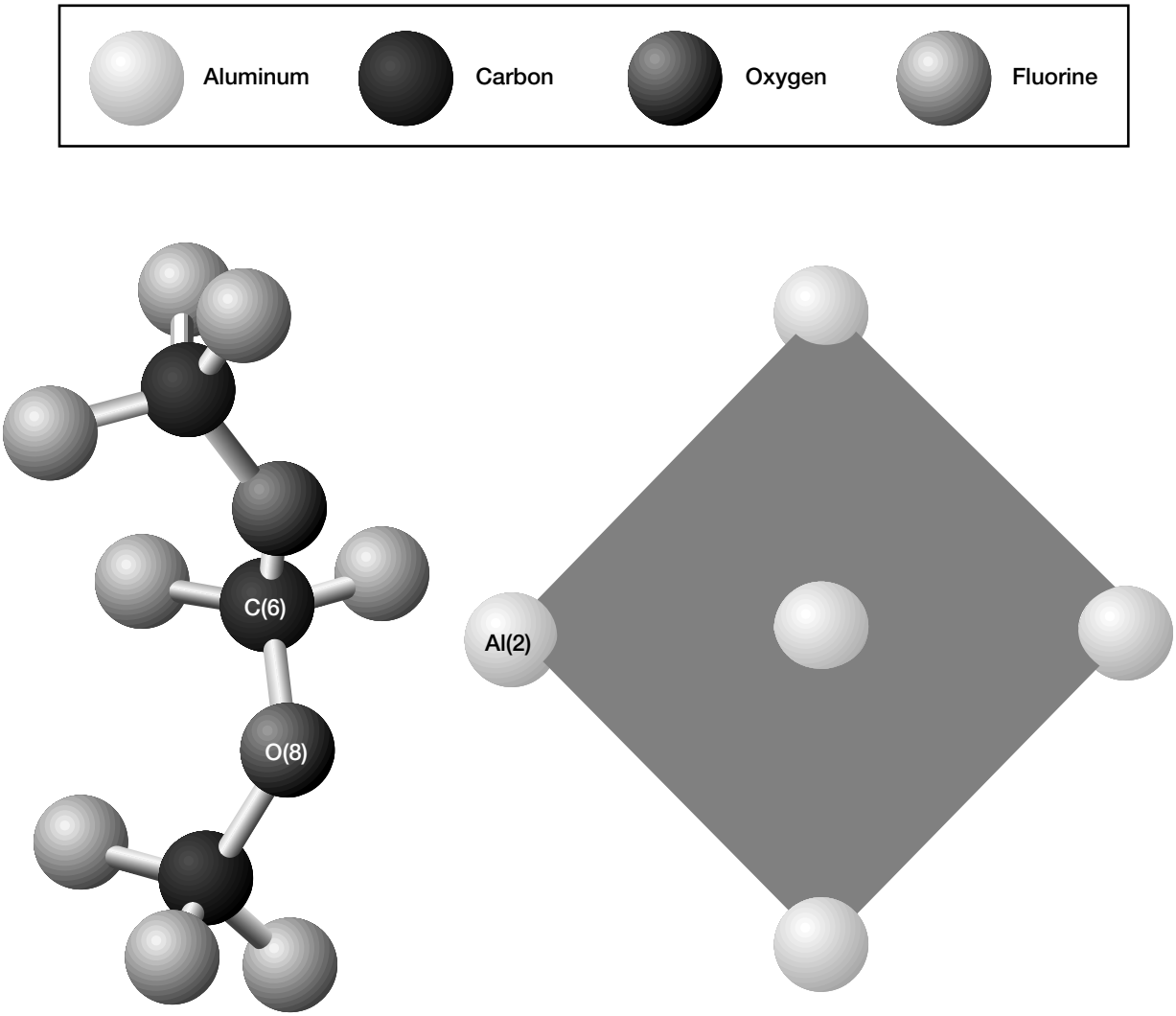

Figure 2.—Five-atom Al cluster/perfluorodimethoxymethane complex: C(6)-Al(2) at 2.60 Å.

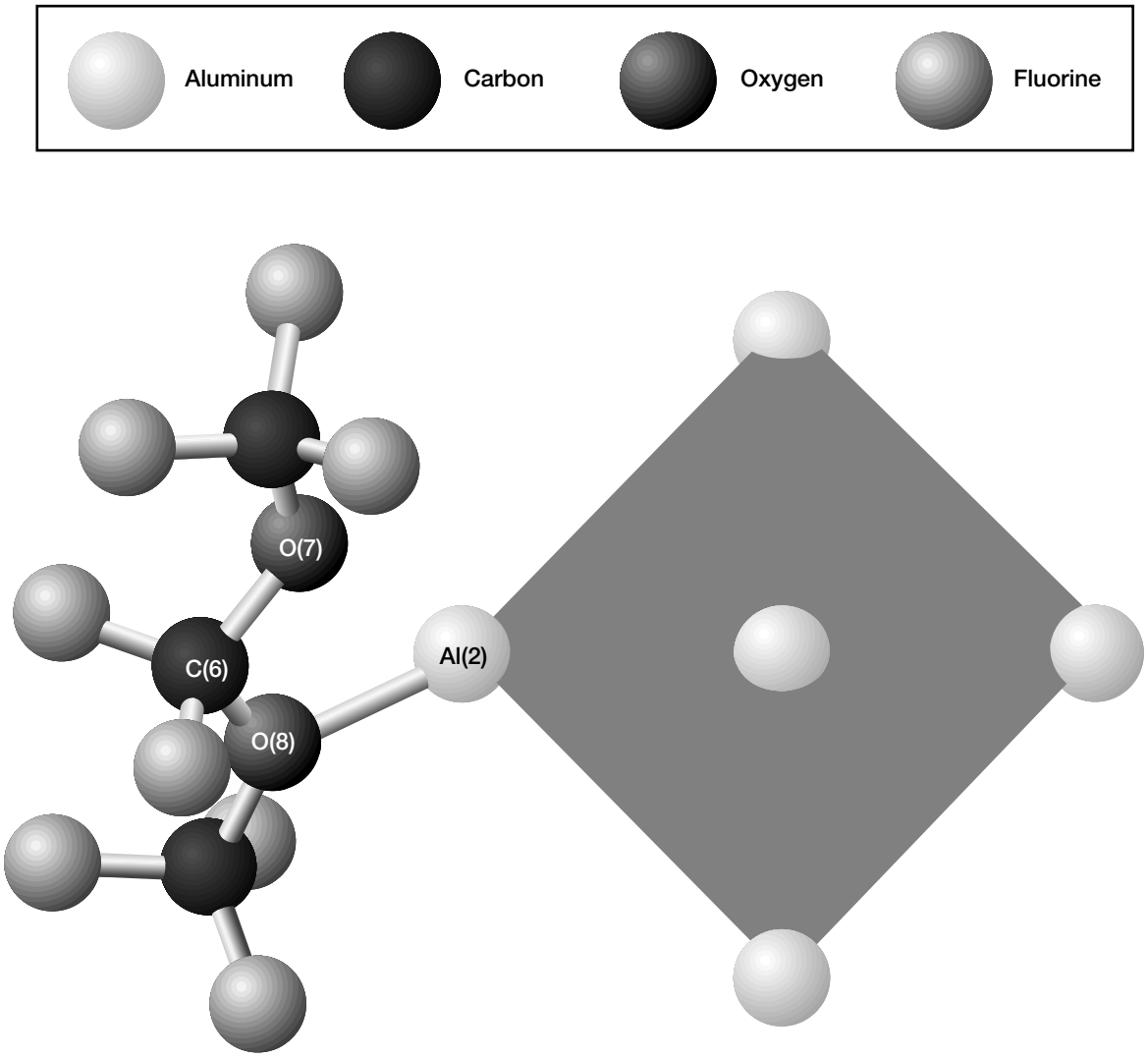

Figure 3.—Five-atom Al cluster/perfluorodimethoxymethane complex: C(6)-Al(2) at 2.57 Å or 2.55 Å.

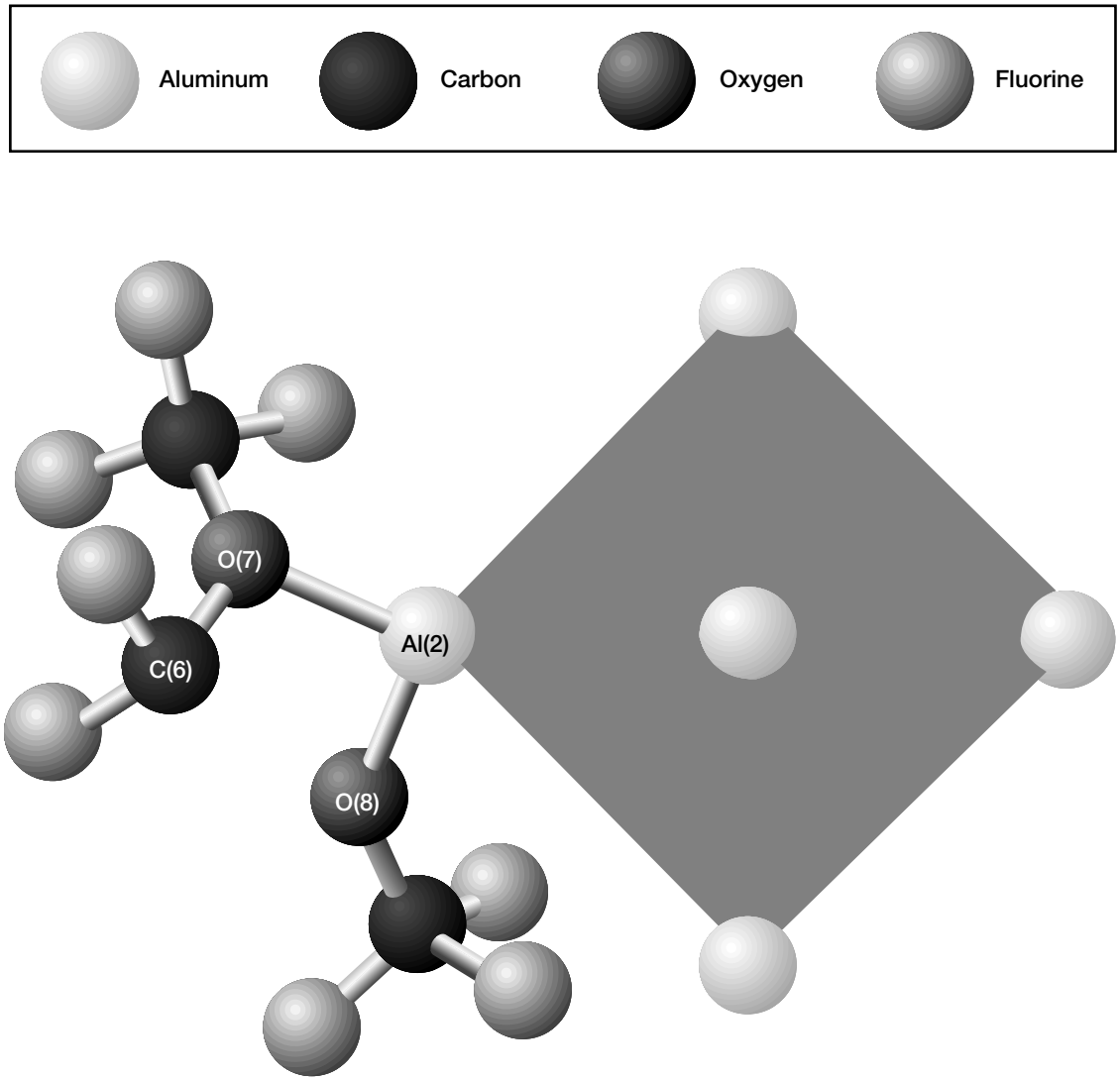

Figure 4.—Five-atom Al cluster/perfluorodimethoxymethane complex: C(6)-Al(2) at 2.53 Å, dissociated ether.

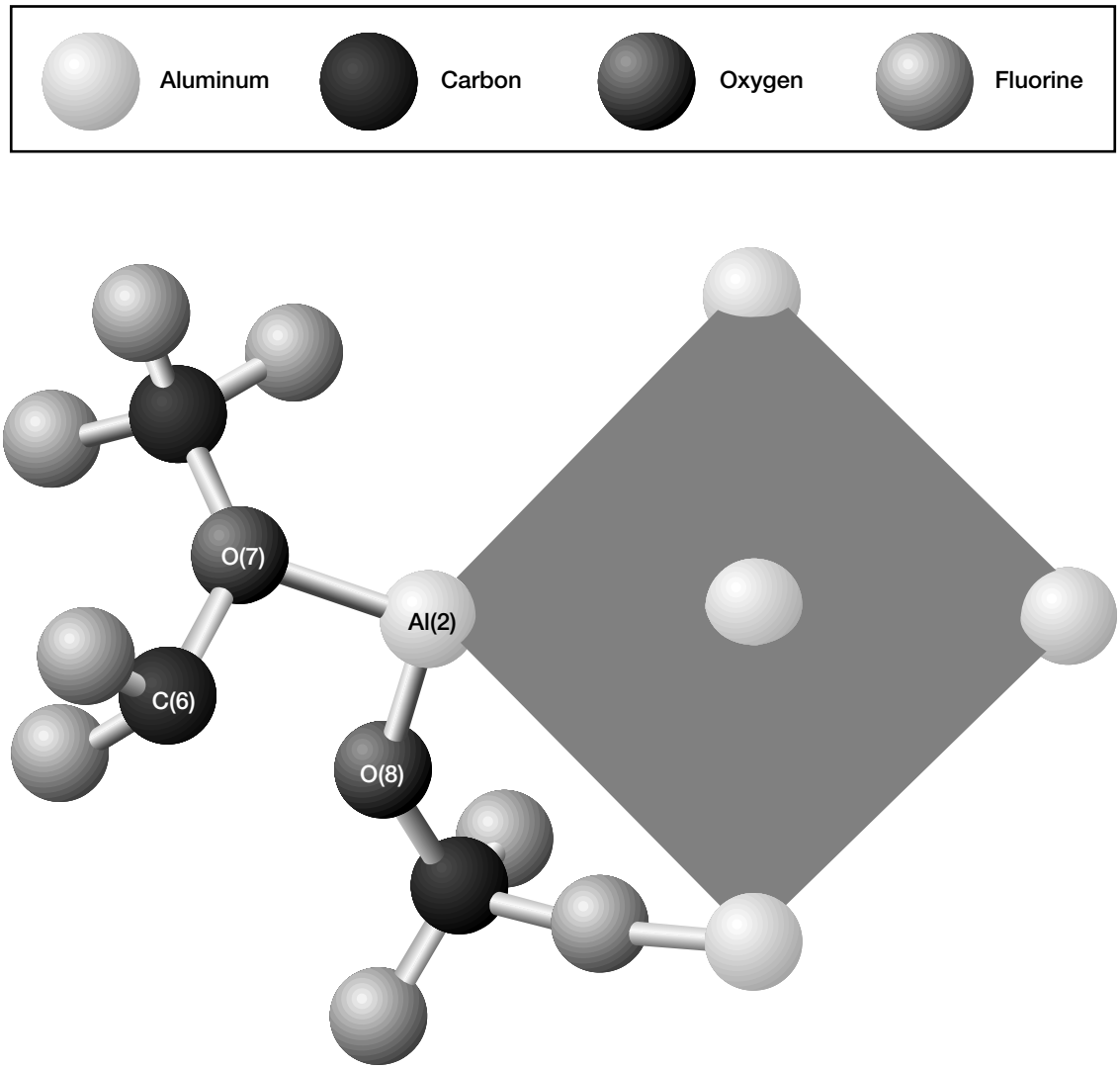

Figure 5.—Five-atom Al cluster/perfluorodimethoxymethane complex: C(6)-Al(2) at 2.50 Å, dissociated ether.

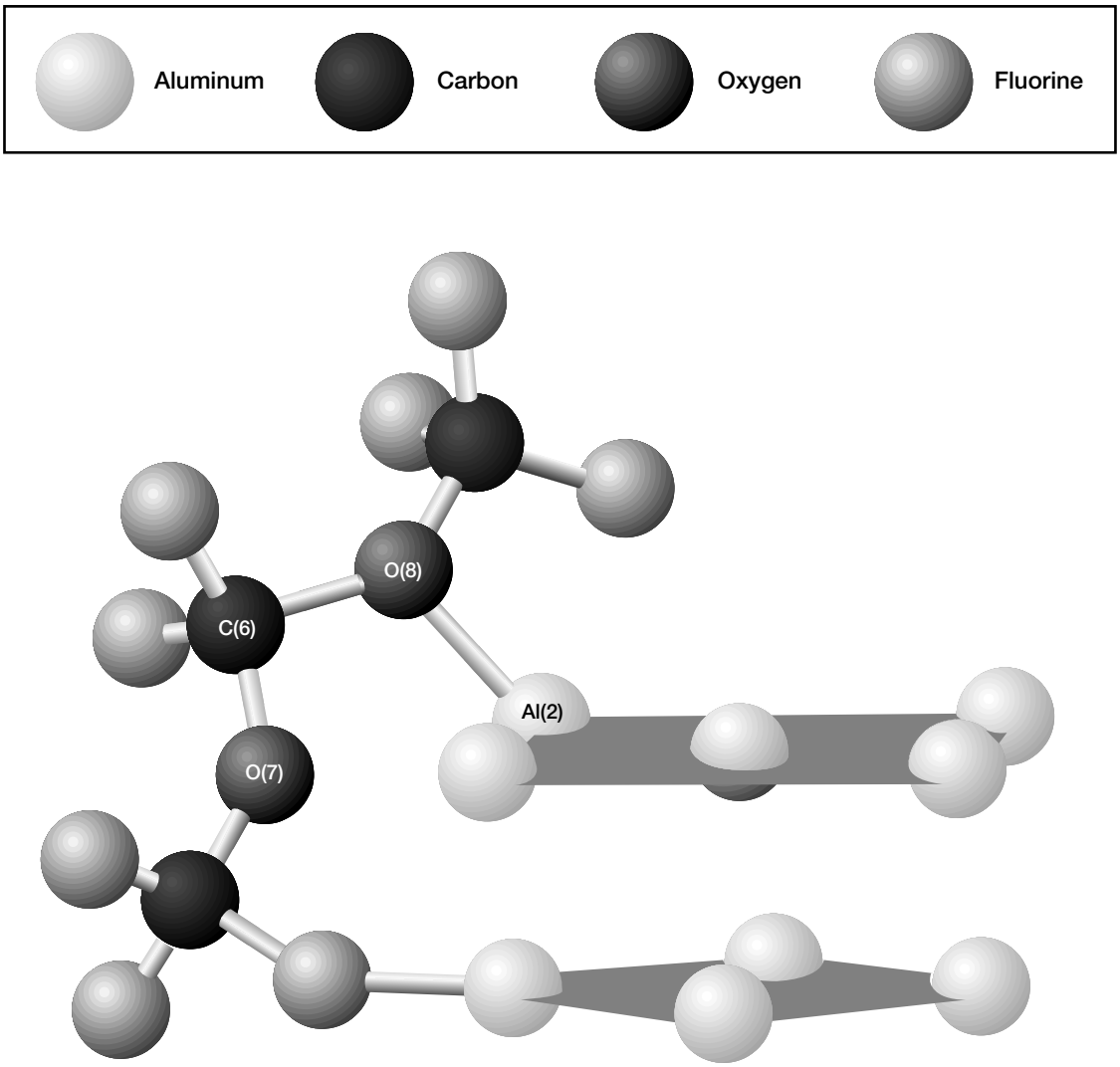

Figure 6.—Nondissociative binding site. Nine-atom Al cluster/perfluorodimethoxymethane complex: edge site.

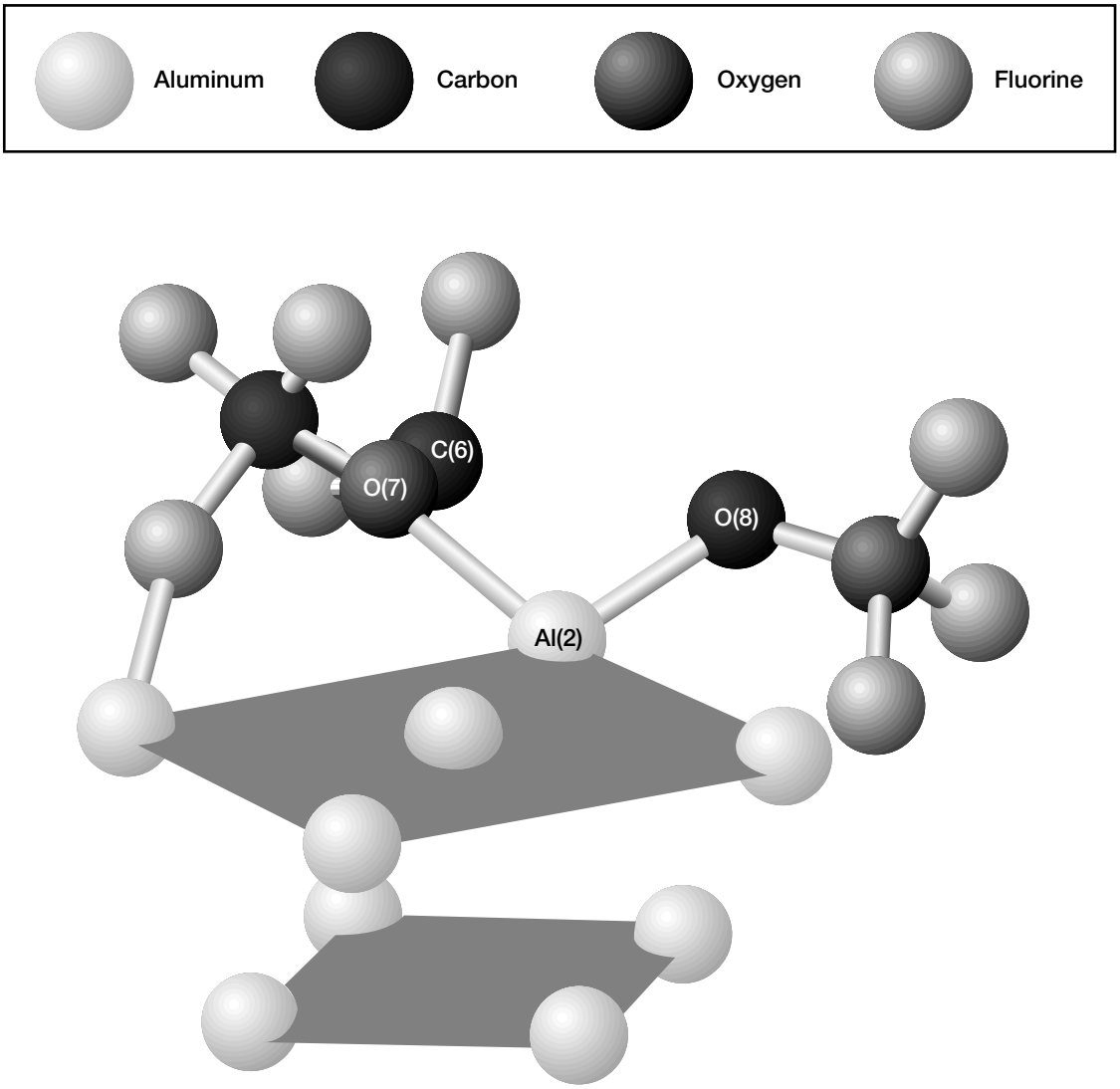

Figure 7.—Dissociative binding site. Nine-atom Al cluster/perfluorodimethoxymethane complex: edge site.

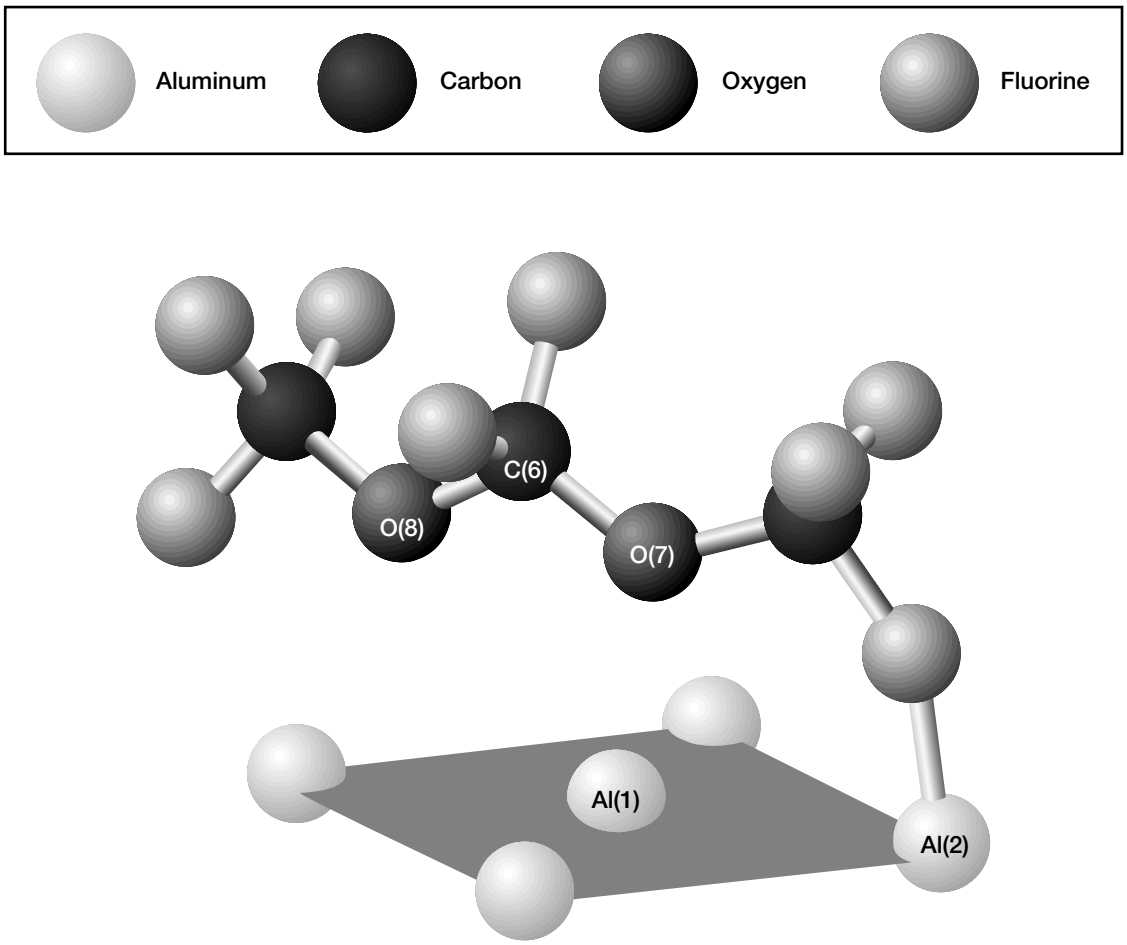

Figure 8.—Nondissociative binding site. Five-atom Al cluster/perfluorodimethoxymethane complex: top site.

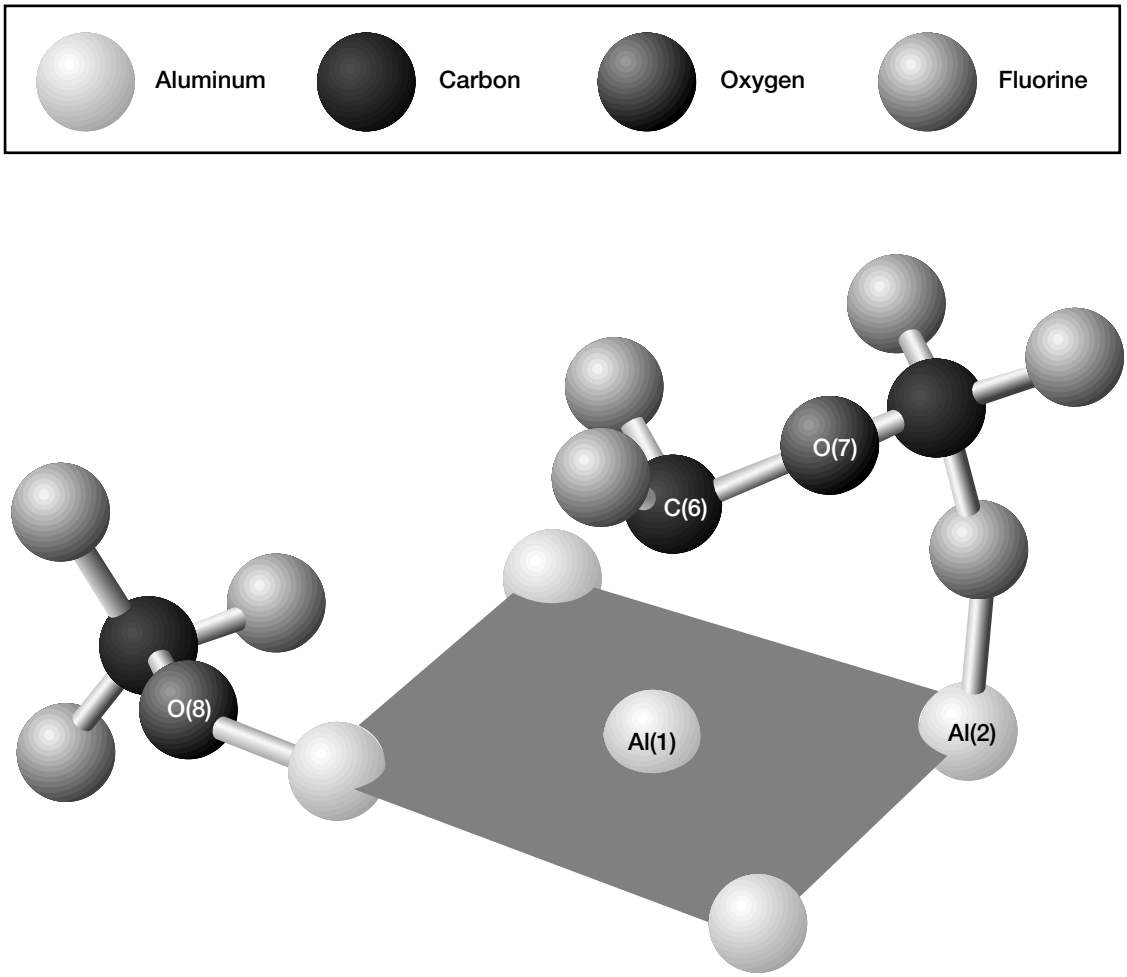

Figure 9.—Dissociative binding site. Five-atom Al cluster/perfluorodimethoxymethane complex: top site.

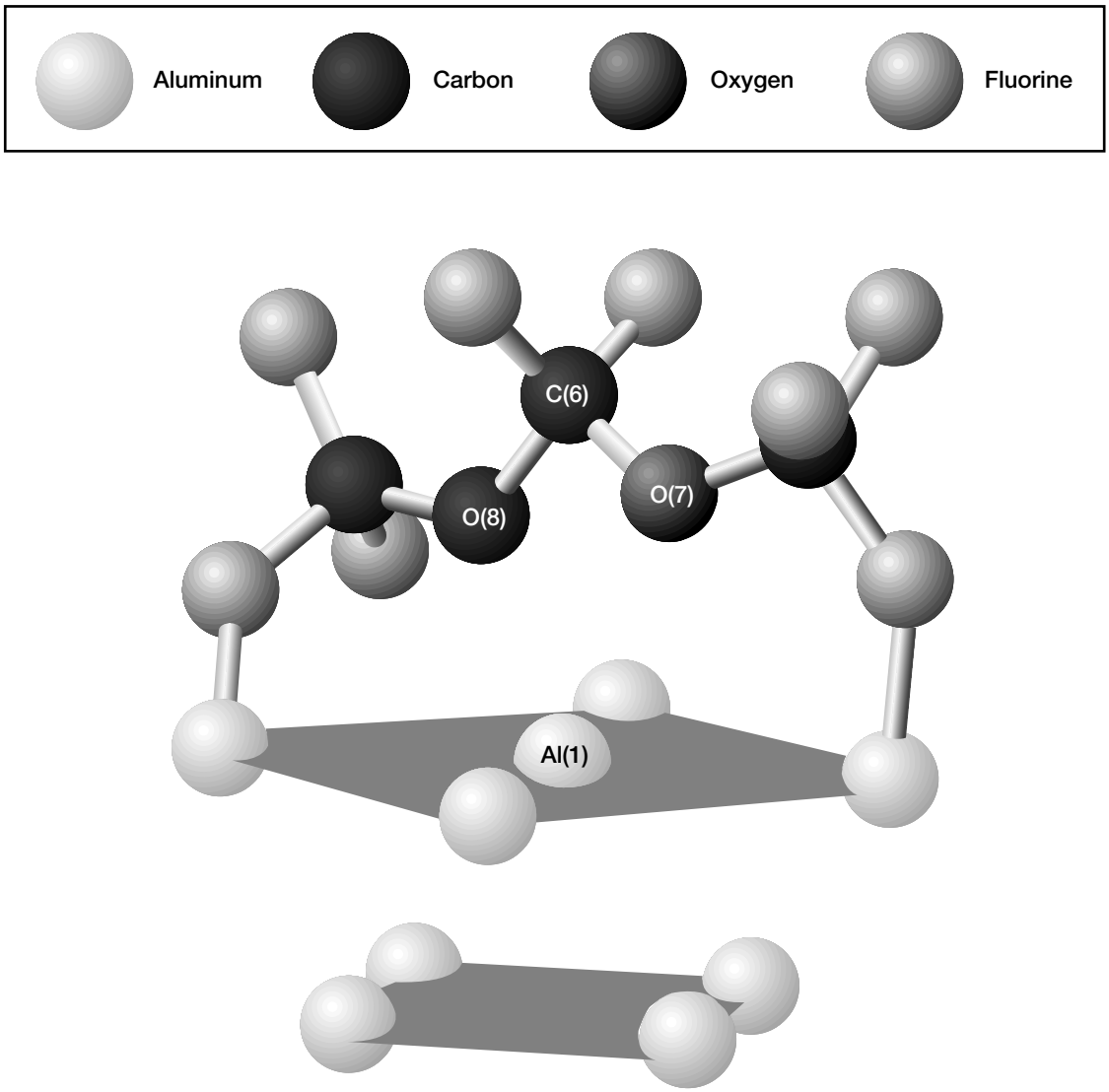

Figure 10.—Nondissociative binding site. Nine-atom Al cluster/perfluorodimethoxymethane complex: top site.

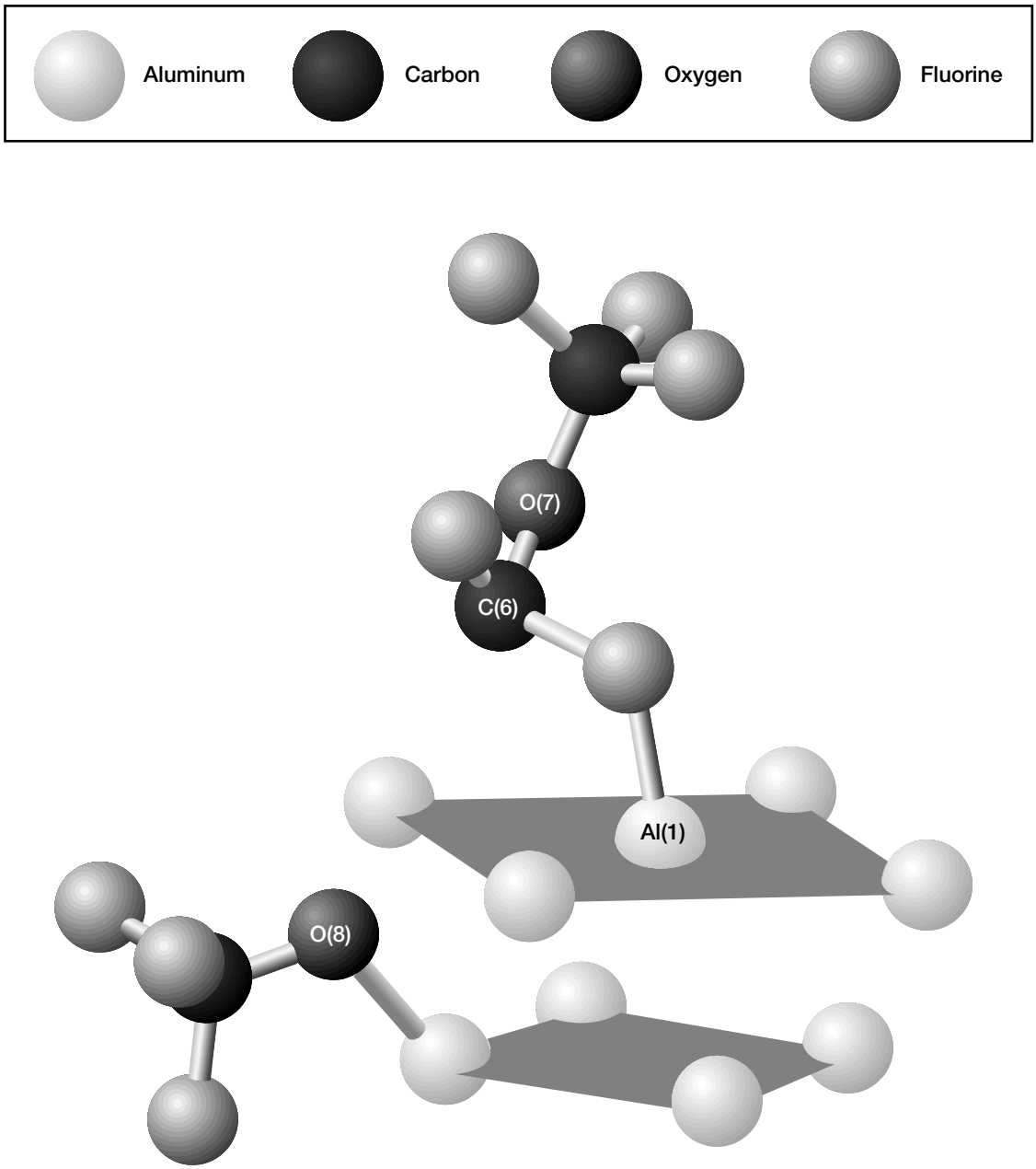

Figure 11.—Dissociative binding site. Nine-atom Al cluster/perfluorodimethoxymethane complex: top site.

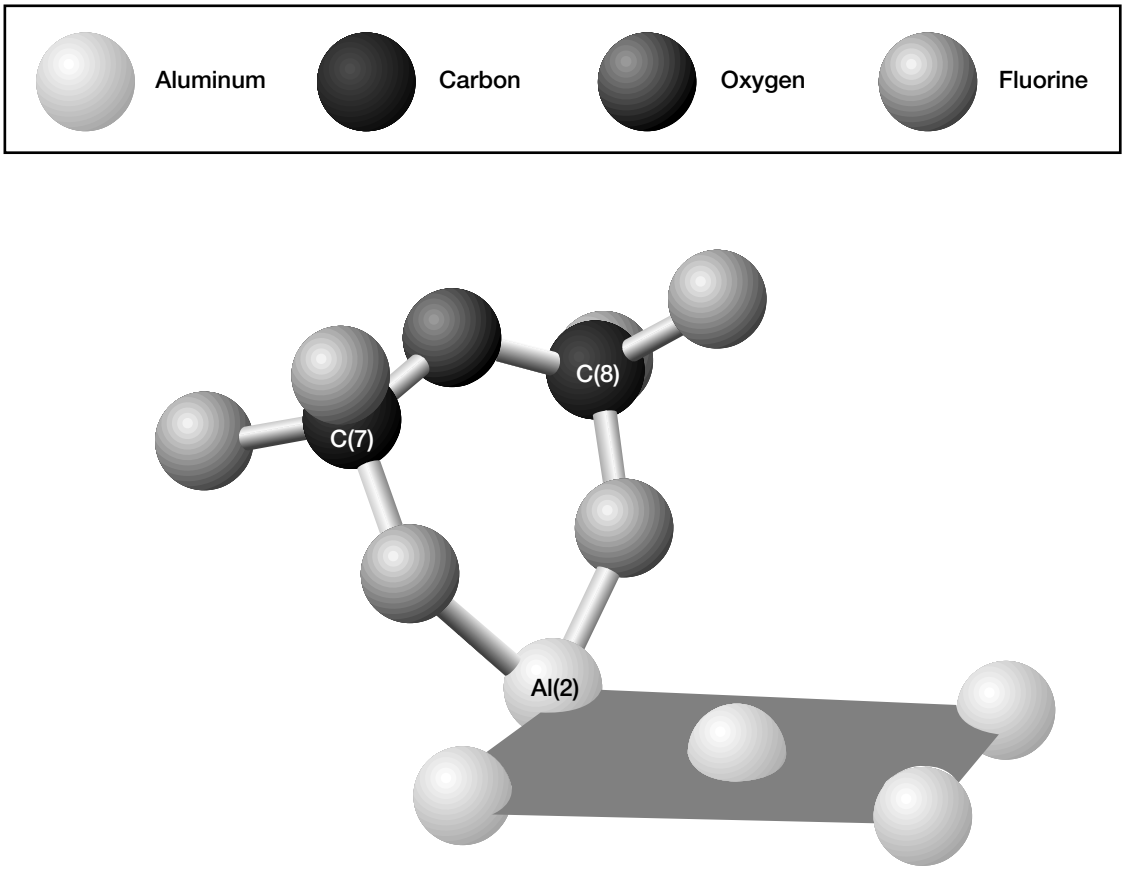

Figure 12.—Nondissociative binding site. Five-atom Al cluster/perfluorodimethyl ether complex: edge site.

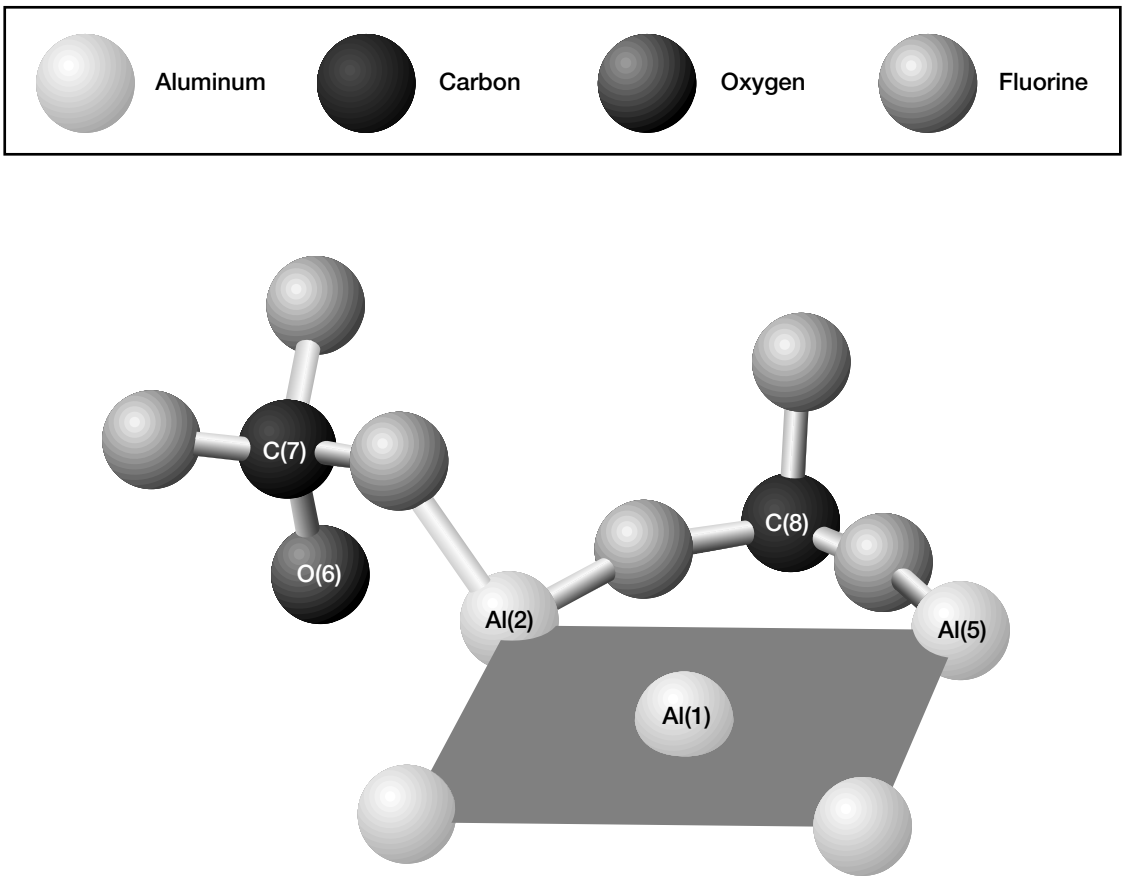

Figure 13.—Dissociative binding site. Five-atom Al cluster/perfluorodimethyl ether complex: edge site.

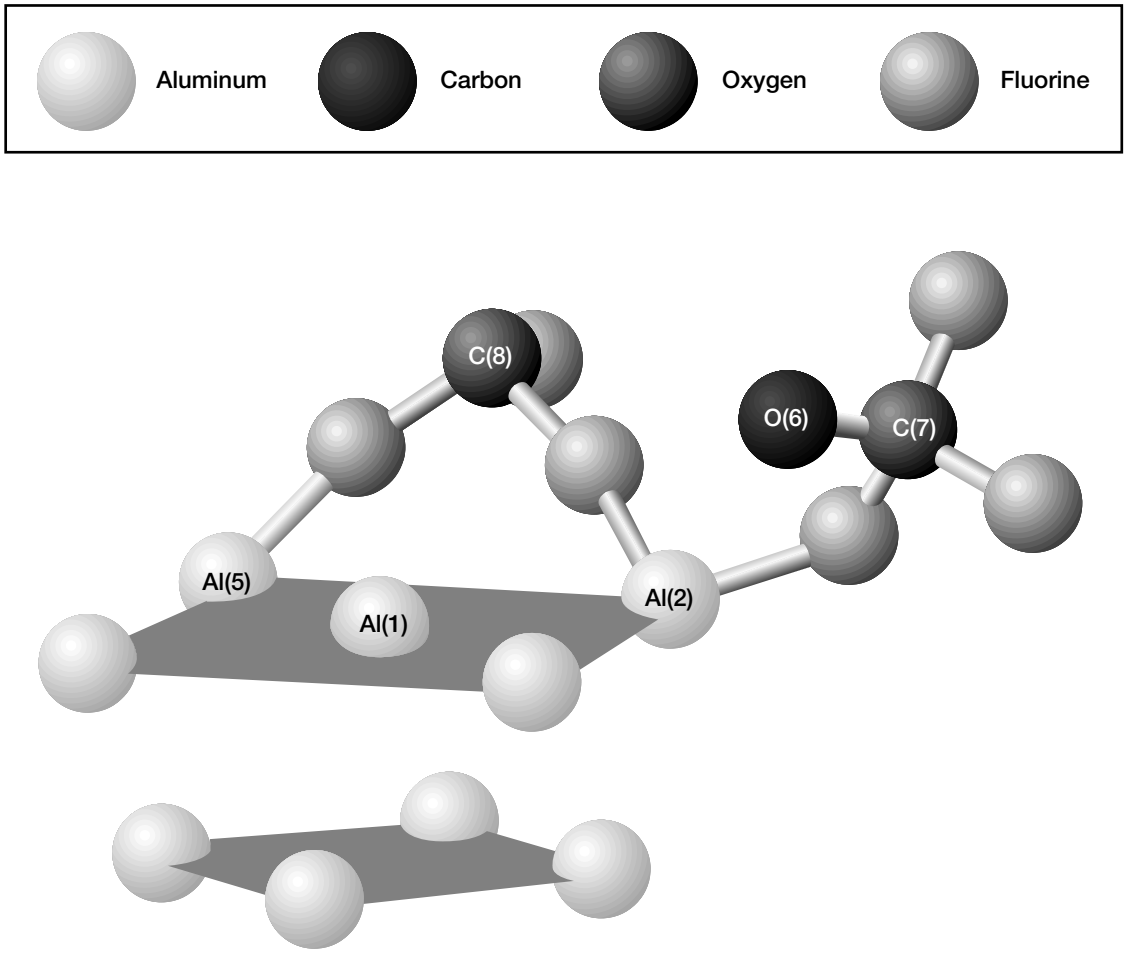

Figure 14.—Dissociative binding site. Nine-atom Al cluster/perfluorodimethyl ether complex: edge site.

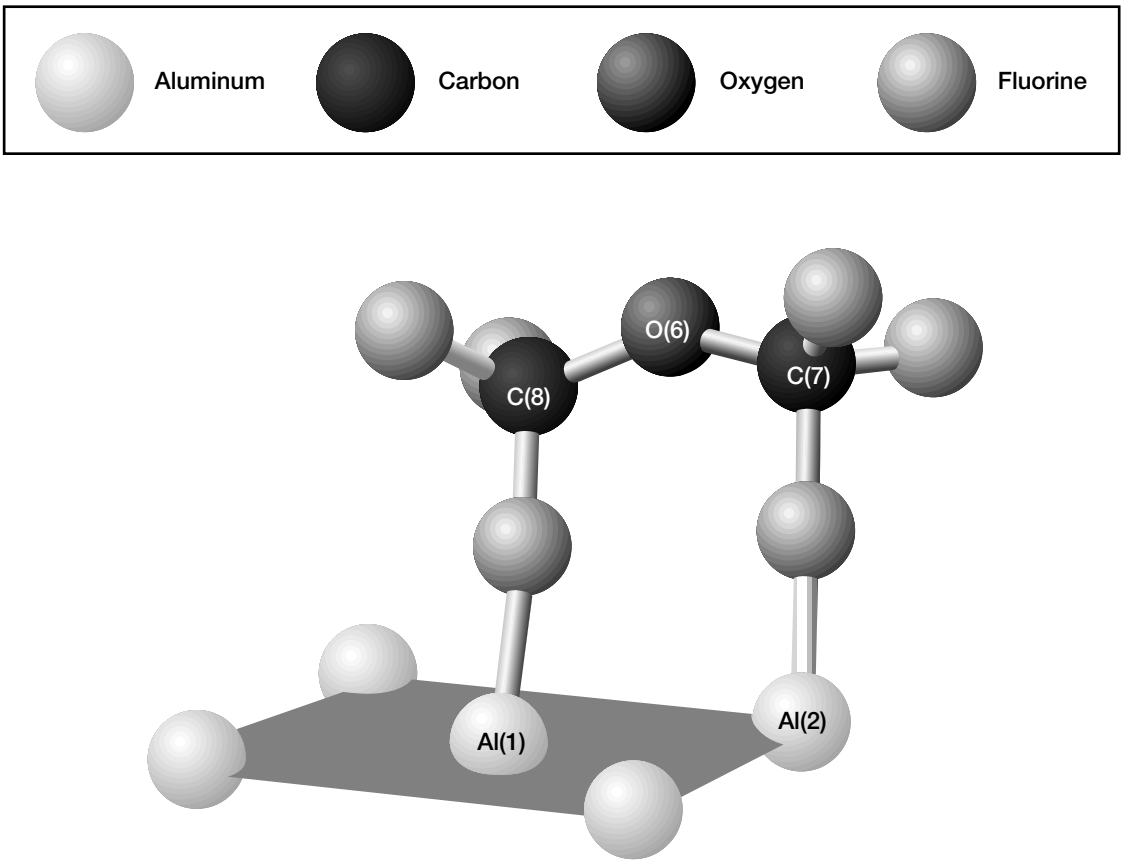

Figure 15.—Nondissociative binding site. Five-atom Al cluster/perfluorodimethyl ether complex: top site.

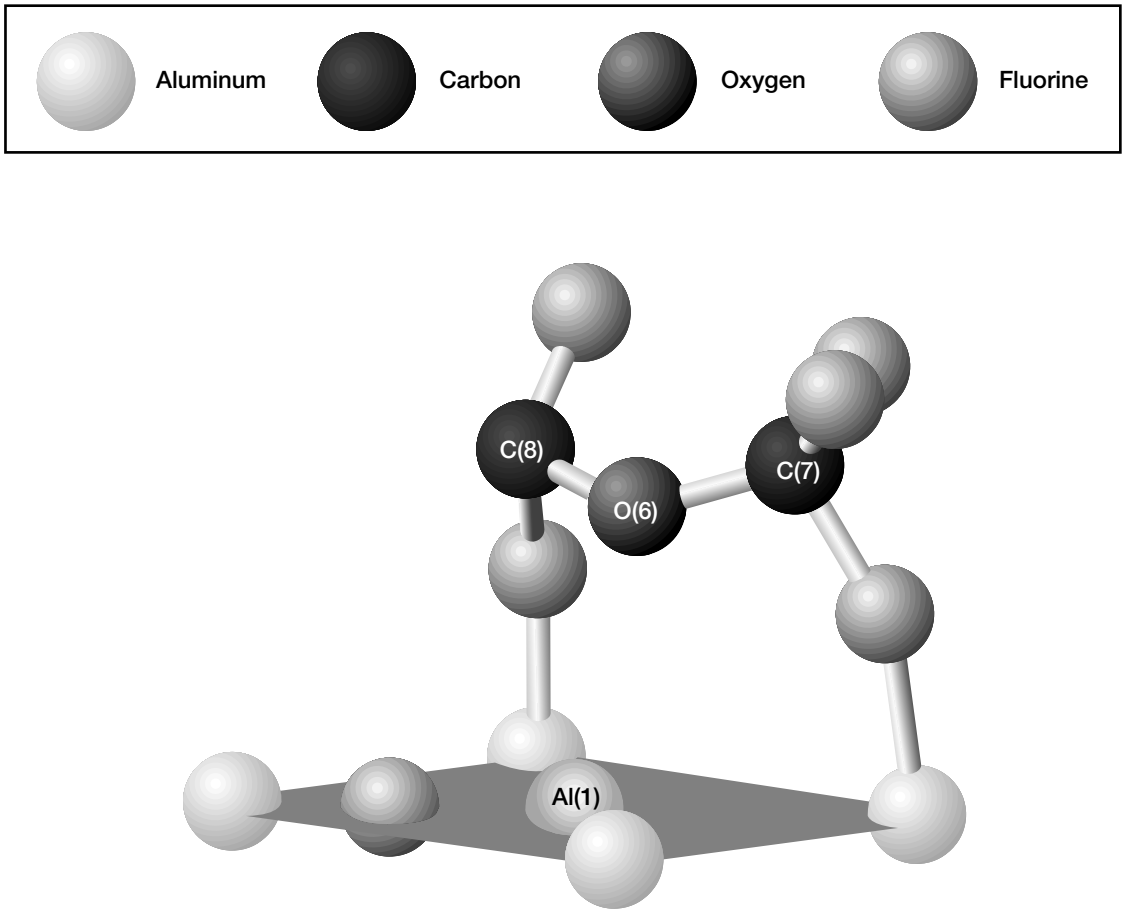

Figure 16.—Nondissociative (with respect to the ether linkage) binding site. Five-atom Al cluster/perfluorodimethyl ether complex: top site. Al(1)-O(6) distance is fixed at 2.50 Å.

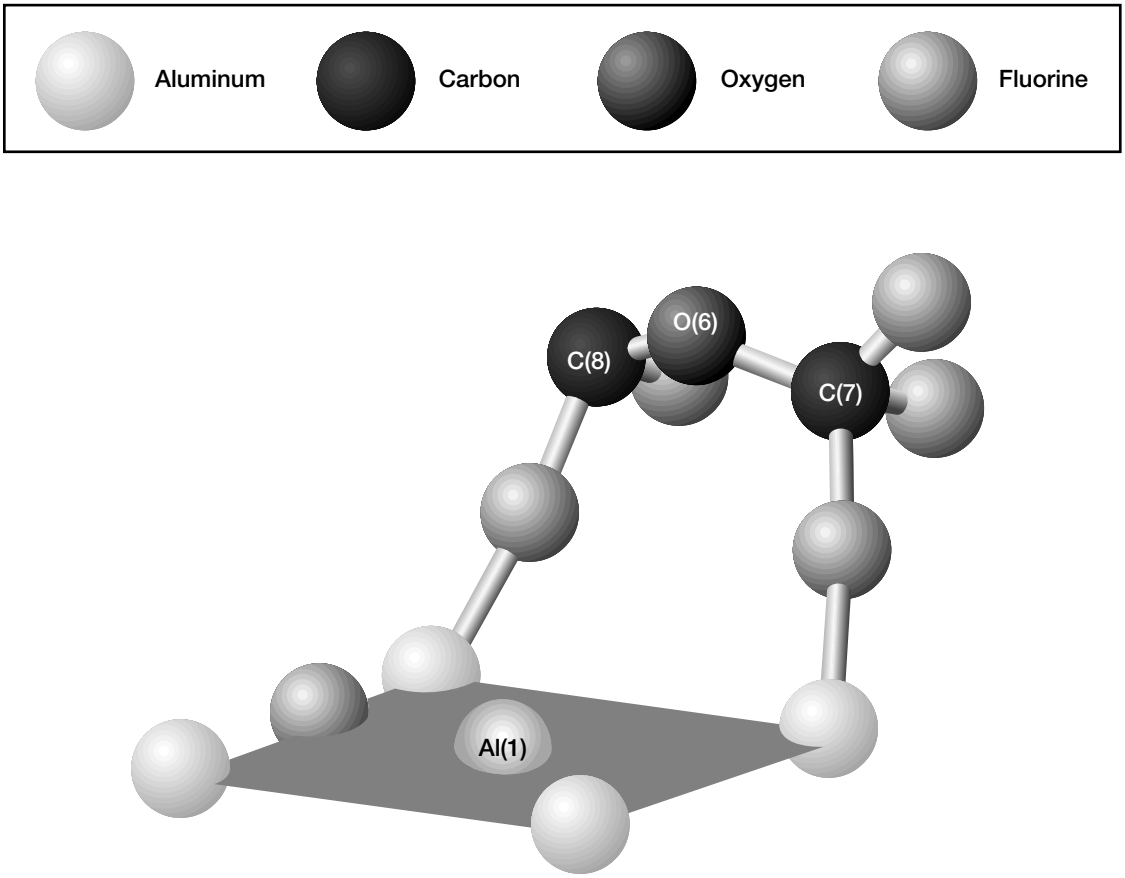

Figure 17.—Nondissociative (with respect to the ether linkage) binding site. Five-atom Al cluster/perfluorodimethyl ether complex: top site. Al(1)-O(6) distance is 4.31 Å.

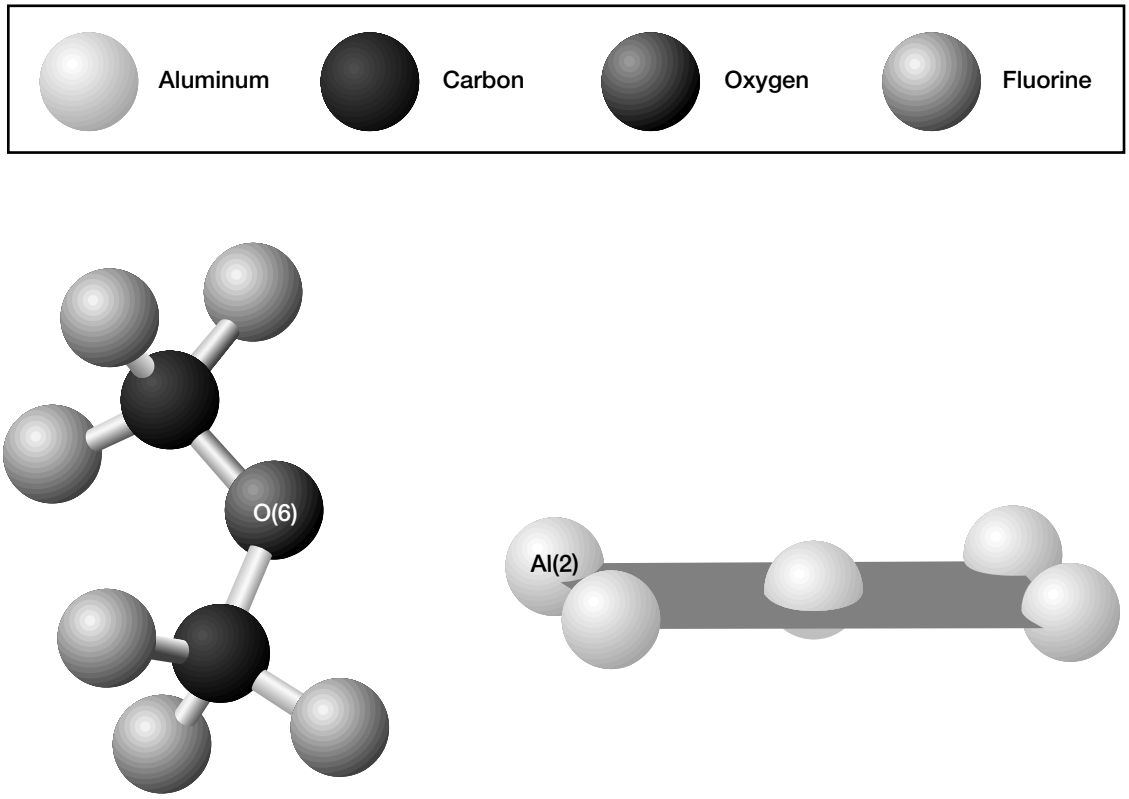

Figure 18.—Nondissociative binding site. Five-atom Al cluster/perfluorodimethyl ether complex: edge site. Ether oxygen directed toward aluminum atoms.

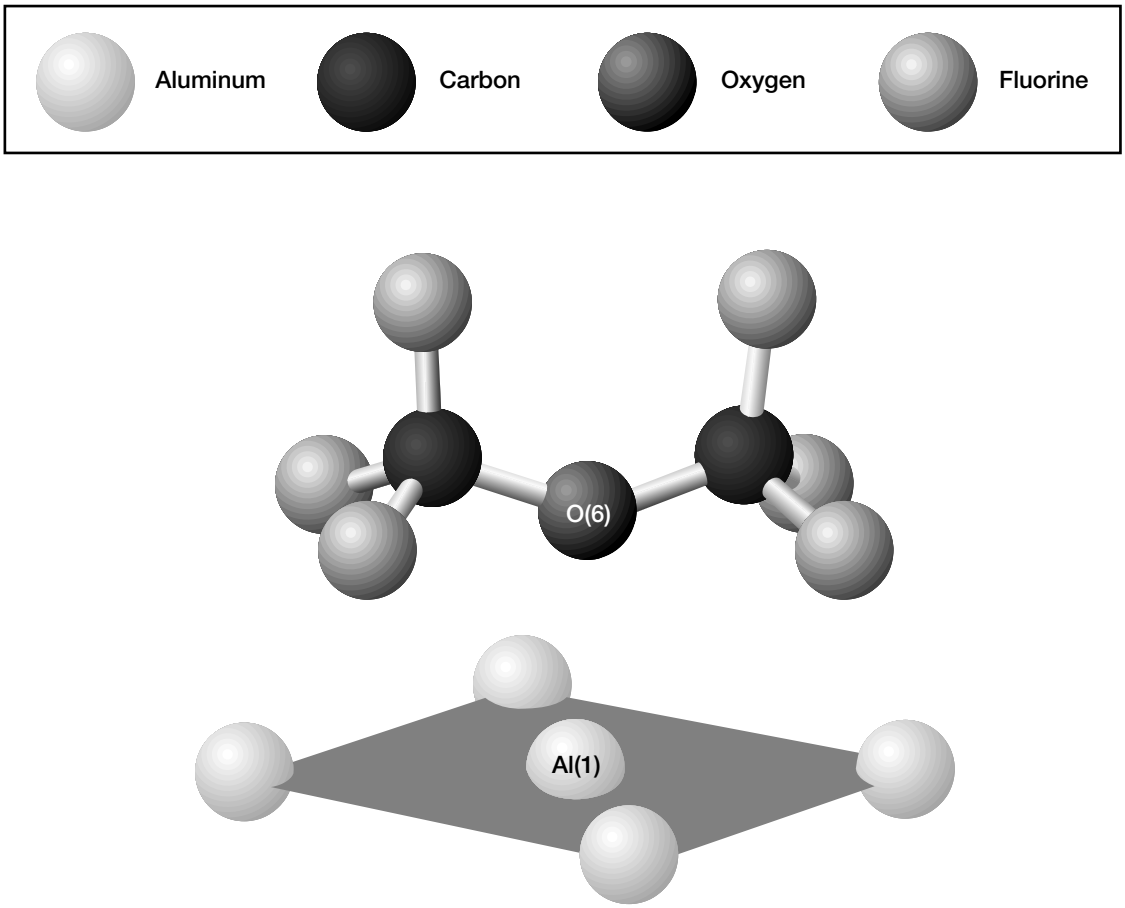

Figure 19.—Nondissociative binding site. Five-atom Al cluster/perfluorodimethyl ether complex: top site. Ether oxygen directed toward aluminum atoms.

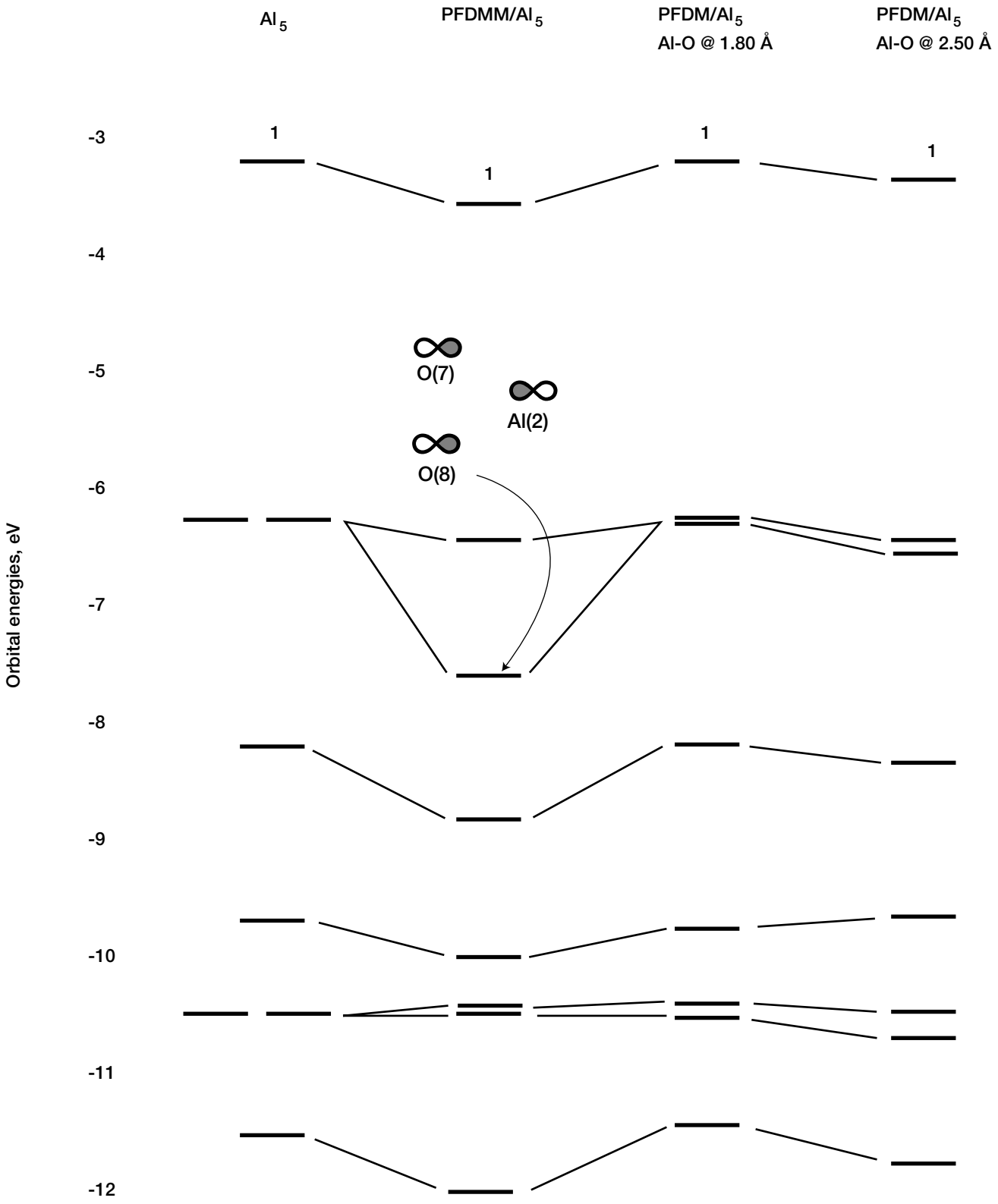

Figure 20.—Comparison of cluster orbital energies for Al_5, PFDMM/Al_5 (fig. 1), and PFDM/Al_5 (fig. 18).

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13. ABSTRACT ***(Maximum 200 words)***

The AM1 semiempirical quantum chemical method was used to model the interaction of perfluoroethers with aluminum surfaces. Perfluorodimethoxymethane and perfluorodimethyl ether were studied interacting with aluminum surfaces, which were modeled by a five-atom cluster and a nine-atom cluster. Interactions were studied for edge (high index) sites and top (low index) sites of the clusters. Both dissociative binding and nondissociative binding were found, with dissociative binding being stronger. The two different ethers bound and dissociated on the clusters in different ways: perfluorodimethoxymethane through its oxygen atoms, but perfluorodimethyl ether through its fluorine atoms. The acetal linkage of perfluorodimeth-oxymethane was the key structural feature of this molecule in its binding and dissociation on the aluminum surface models. The high-index sites of the clusters caused the dissociation of both ethers. These results are consistent with the experimental observation that perfluorinated ethers decompose in contact with sputtered aluminum surfaces.

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