Virginia Commonwealth University
VCU Scholars Compass

Physics Publications

Dept. of Physics

1999

Structure and stability of the AlX and AlX- species

Gennady L. Gutsev
Virginia Commonwealth University

Puru Jena
Virginia Commonwealth University

Rodney J. Bartlett
University of Florida

Follow this and additional works at: http://scholarscompass.vcu.edu/phys_pubs

Part of the Physics Commons

Downloaded from

http://scholarscompass.vcu.edu/phys_pubs/145

Structure and stability of the AlX and AlX⁻ species

Gennady L. Gutsev[a)] and Puru Jena
Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

Rodney J. Bartlett
Quantum Theory Project, P. O. Box 118435, University of Florida, Gainesville, Florida 32611-8435

The electronic and geometrical structures of the ground and low-lying excited states of the diatomic AlX and AlX⁻ series (X=H, Li, Be, B, C, N, O, and F) are calculated by the coupled-cluster method with all singles and doubles and noniterative inclusion of triples using a large atomic natural orbital basis. All the ground-state AlX molecules except for AlF can attach an additional electron and form ground-state AlX⁻ anions. The ground-state AlBe⁻, AlB⁻, AlC⁻, AlN⁻, and AlO⁻ anions possess excited states that are stable toward autodetachment of an extra electron; AlBe⁻ also has a second excited state. Low-lying excited states of all AlX but AlN can attach an extra electron and form anionic states that are stable with respect to their neutral (excited) parent states. The ground-state AlLi⁻, AlBe⁻, AlB⁻, AlN⁻, and AlO⁻ anions are found to be thermodynamically more stable than their neutral parents. The most stable is AlO⁻, whose dissociation energy to Al+O⁻ is 6.4 eV. Correspondingly, AlO possesses the largest electron affinity (2.65 eV) in the series. © *1999 American Institute of Physics.* [S0021-9606(99)30606-1]

I. INTRODUCTION

It was found recently,[1] on the basis of experimental and most reliable theoretical data, that the ground states of the *sp* diatomic molecules exhibit a definite periodicity along the rows and columns of the diatomic ''periodic'' table[2] that resembles that of atoms obeying Hund's rule. It is not clear if a similar periodicity exists for diatomic anions, since experimental data and results of reliable calculations are scarce.

The attachment of an additional electron is a rather complicated process. For example, a neutral molecule in some excited state can attach an extra electron and form an anion state that is stable with respect to its parent state, although the ground-state molecule cannot attach an extra electron. AlF seems to offer such an example, as it does not attach an additional electron in its ground state $^1\Sigma^+$, but can attach an extra electron in its excited $^3\Pi$ state and form a $^4\Sigma^-$ anionic state[3] metastable with respect to the neutral $^1\Sigma^+$ state. Another example is the $\mathrm{He}_2^-(^4\Pi_g)$ anion, which is stable with respect to its neutral parent $\mathrm{He}_2(^3\Sigma_u)$ excited state,[4] whereas the ground $^1\Sigma^+$ state of He_2 is extremely weakly bound [only by 1 mK (Ref. 5)] and cannot attach an extra electron. On the other hand, some anions can have several excited states that are stable toward autodetachment of an extra electron or, in other words, whose total energies are below the total energy of the neutral parent ground state. For example, AlP⁻ has been computed to have up to seven states below the ground state of AlP.[6]

The neutral AlX species (X=from H to F) have been the subject of many theoretical investigations[1] performed at different levels and with various basis sets. The most popular molecule appears to be AlH, which serves as a benchmark system.[7–24] The open-shell species from AlLi to AlO have received somewhat less attention,[25–40] while the closed-shell molecule AlF has been the subject of numerous studies.[41–54] Some first-order properties have been calculated for AlH,[7,12,13,20,21] AlC,[28] AlO,[32] and AlF.[41,45,49]

The adiabatic electron affinities ($A_{ad}s$) have been estimated for AlH,[22–24] AlLi,[25] AlBe,[26] and AlO.[38] The only experimental value, to the best of our knowledge, is available for the A_{ad} of AlO.[55,56] The dissociation energies have been calculated for AlH⁻,[7] AlLi⁻,[25] AlBe⁻,[26] and AlO⁻,[38] as well as for an excited state of AlF⁻.[3] No experimental data have been reported on the structure of the AlX⁻ anions.

The aim of the present work is to consider the ground and lowest excited states of neutral and negatively charged diatomic species formed by Al and second-row atoms at the same level of theory: the infinite-order coupled-cluster method with all singles and doubles and noniterative inclusion of triple excitations [CCSD(T)] using a large atomic natural orbital basis. In the following, we assign the symmetry of the anionic ground states, define the adiabatic electron affinities of AlX, evaluate dissociation energies of the neutral and anionic ground states, and determine first-order properties for the ground-state AlX molecules.

II. COMPUTATIONAL DETAILS

Our calculations have been performed with the ACES II suite of programs[58] at the CCSD(T)[59] level for diatomic species and the CCSDT (with the iterative inclusion of triple excitations[60]) level for atoms. A large atomic natural orbital basis of Widmark–Malmqvist–Roos (WMR)[61] consisting of $[8s4p3d/6s4p3d]$ for H, $[14s9p4d3f/7s6p4d3f]$ for Li, $[14s9p4d3f/7s7p4d3f]$ for Be to F, and $[17s12p5d4f/7s7p5d4f]$ for Al is employed.

The A_{ad} of a molecule can be defined as the difference in the total energies of an anion state and the supporting state of the neutral parent. Within the Born–Oppenheimer approximation, one may define the A_{ad} as

$$A_{ad} = E_{tot}(N, R_e) + Z_N - E_{tot}(A, R_e^-) - Z_A$$
$$= \Delta E_{el} + \Delta E_{nuc}, \qquad (1)$$

where R_e and R_e^- denote the equilibrium geometrical configurations of the neutral molecule and the anion, respectively. The zero-point vibrational energies (Z) are estimated within the harmonic approximation. Dissociation energies are evaluated as

$$D_0 = E_{tot}(AB) + Z_{AB} - E_{tot}(A) - E_{tot}(B). \qquad (2)$$

First-order properties can be computed as expectation values of corresponding operators or via perturbation theory.[62–64] These two approaches are equivalent in the case of exact wave functions. In ACES II, first-order properties are evaluated analytically using the energy-derivative formalism,[62,65] which introduces the ''response'' and ''relaxed'' density matrices of coupled-cluster (CC) theory.

III. RESULTS AND DISCUSSIONS

A. Structure of anions

The ground states of AlH, AlC, AlN, AlO, and AlF have been determined experimentally,[50,51] whereas the ground states of AlLi, AlBe, and AlB have been obtained from the results of nonempirical calculations.[1] A compilation of the results of our calculations and those of others, together with experimental data, is displayed in Table I. As is seen, the CCSD(T)/WMR level allows a rather accurate description of experimental spectroscopic constants.

Theoretical assignment of the AlX ground states coincides with the experimental data for all the molecules except for AlN, for which the $X\,^3\Pi - A\,^3\Sigma^-$ splitting was found to be positive (371 cm^{-1}) in multireference configuration interaction (MRCI) calculations with a $6s5p2d1f$ basis.[30] Our CCSD(T)/WMR result decreases the separation to 20 cm^{-1}, and quadruple excitations or higher-l basis functions would seem to be important to reverse the splitting and obtain the experimentally derived ground state $X\,^3\Pi$.

It has been pointed out by many authors[67–71] that diatomic molecules favor high-spin ground-state configurations as do atomic anions.[71] As is seen from Table II, the ground states of the AlX$^-$ anions follow the same trend as their neutral parents, and the ground states of the anions are the same as those of their isoelectronic neutral species.

Low-lying excited states of the AlX species have been computed at different levels of theory (see references in Table I), and their spectroscopic constants obtained at the CCSD(T)/WMR level are presented in Table I, together with the data of other correlated computations. Leading electronic configurations of anionic states have been tested by adding an extra electron to the leading configurations of the corresponding neutral excited states. An anion state is considered to exist if its total energy is below the total energy of the parent state. Table I contains the results of our search for

bound anionic states and also presents several unbound states for those cases where we have not succeeded in finding a bound state (see, e.g., AlN$^-$).

B. Adiabatic electron affinity

To assess the accuracy to be anticipated for the CCSD(T)/WMR level, we have calculated the electron affinities (EAs) of atoms entering the AlX species, since these EAs have been measured with high accuracy. Comparison of our values with the experimental data[73,74] made in the uppermost panel of Table II shows that the largest discrepancy of 0.1 eV is observed for the EA of the oxygen atom, where higher excitations[75] or higher angular momenta basis functions[76] appear to be important.[75] Note that the CCSD(T) and CCSDT levels provide rather similar values.

The Be and N atoms are known to have no affinity to the extra electron attachment, and consequently their computed EAs are negative. Their relatively large absolute magnitudes can be traced to a rather confined character of the WMR basis, which precludes simulating autodetachment of an extra electron via coupling to the continuum.[77,78] On the basis of our estimates of the atomic EAs and our previous calculations on the A_{ad} of NH,[75] one could anticipate the accuracy in estimating the AlX A_{ad}s to be within ~0.1 eV.

The A_{ad}s are computed according to Eq. (1). However, the Z corrections were found not to exceed 0.01 eV and are unnecessary. As follows from the middle panel of Table II, all the ground-state AlX species, except for AlF, are able to attach an extra electron. Remarkably, all the ground-state anions except for AlH$^-$ and AlF$^-$ are stable toward autodetachment, even at the Hartree–Fock (HF) level (contrary to the atomic case, where only C$^-$ and F$^-$ are stable at the HF level). The AlF$^-$ ($^2\Pi$) anion is found to be unstable toward autodetachment at the CCSD(T)/WMR level, which is in agreement with a previous result[3] obtained from MBPT(4)/6-31+G(d) calculations. Our computed A_{ad} s of AlH, AlLi, and AlBe are in good accord with the results of other high-quality calculations.[22–25,27] A relatively large discrepancy between our value of the A_{ad} of AlO and that obtained by Peterson and Woods[38] appears to be due to the way they estimate the A_{ad}. They have obtained an overestimated dissociation energy of AlO$^-$ by ≈ 0.5 eV and used this energy in the relation $A_{ad}(AlO) = D_0(AlO^-) + A(O) - D_0(AlO)$, where the experimental values have been substituted for $A(O)$ and $D_0(AlO)$. Our computed value of 2.65 eV for the A_{ad} of AlO is in excellent agreement with the recently measured experimental value of 2.6 eV.[55,56]

Similar to the atomic case, the A_{ad} behavior is not monotonic when moving from AlH to AlF. The A_{ad} increases first, then drops down at AlC, then increases again and drops down at AlF. AlC can be considered an analog to the N or P atoms, because all of them have three p-type valence electrons, and AlF can be considered an analog to the noble gas Ne or Ar atoms, because of having six p-type valence electrons. AlBe$^-$, AlB$^-$, AlC$^-$, AlN$^-$, and AlO$^-$ are found to have excited states whose total energies are below those of their ground-state parents. The AlBe$^-$ anion also possesses a

TABLE I. Spectroscopic constants [equilibrium bond lengths R_e (in Å), vibrational frequencies ω_e (in cm^{-1}), and rotational constants B_e (in cm^{-1})] of the AlX and AlX$^-$ series. The results of this work (tw) are obtained at the CCSD(T)/WMR level. Total energies (in hartrees) obtained in other theoretical studies are chosen to be those which are computed at the highest level of theory in a corresponding source paper. Our spin multiplicities are calculated with the CCSD(T) density according to Ref. 66.

Species	State	Ref.	R_e	ω_e	B_e	E_{tot}	$\langle 2S+1\rangle$
AlH	$^1\Sigma^+$ $(5\sigma^2 1\pi^4)$	tw	1.6399	1690	6.45	−242.687 708	1.0
		7	1.645	1692	6.41	−242.557 486	1.0
		12	1.652	1677	⋯	−242.539 778	1.0
		15	1.653	1683	⋯	⋯	1.0
		18	1.6533	1680	6.35	−242.550 12	1.0
		Exp. 50	1.6478	1683	6.39	⋯	⋯
AlH	$^3\Pi$ $(5\sigma^1 2\pi^1)$	tw	1.5868	1811	6.89	−242.617 524	3.000
AlH$^-$	$^2\Pi$ $(5\sigma^2 2\pi^1)$	tw	1.6746	1512	6.18	−242.693 286	2.002
		22	1.696	1485	6.03	−242.558 11	⋯
		23	1.689	1573	⋯	−242.427 95	⋯
AlH$^-$	$^4\Sigma^-$ $(5\sigma^1 2\pi^2)$	tw	1.5978	1778	6.79	−242.645 473	4.000
AlLi	$^1\Sigma^+$ $(6\sigma^2 1\pi^4)$	tw	2.8381	316	0.376	−249.570 424	1.0
		Exp. 52	⋯	318	⋯	⋯	⋯
		25	2.869	322	⋯	⋯	⋯
AlLi	$^3\Pi$ $(6\sigma^1 2\pi^1)$	tw	2.6186	346	0.442	−249.562 290	3.007
		25	2.623	351	⋯	⋯	⋯
AlLi$^-$	$^2\Pi$ $(6\sigma^2 2\pi^1)$	tw	2.8346	264	0.377	−249.594 430	1.996
		25	2.832	268	⋯	⋯	⋯
AlLi$^-$	$^4\Sigma^-$ $(6\sigma^1 2\pi^2)$	tw	2.5448	341	0.467	−249.586 830	4.003
		25	2.438	461	⋯	⋯	⋯
AlBe	$^2\Pi$ $(6\sigma^2 2\pi^1)$	tw	2.3981	395	0.434	−256.740 274	2.001
		26	2.427	309	⋯	⋯	⋯
AlBe	$^2\Sigma^+$ $(7\sigma^1 1\pi^4)$	tw	2.6009	327	0.369	−256.734 857	2.004
		26	2.632	309	⋯	⋯	⋯
AlBe	$^4\Sigma^-$ $(6\sigma^1 2\pi^2)$	tw	2.1057	614	0.563	−256.699 821	4.006
AlBe$^-$	$^3\Sigma^-$ $(6\sigma^2 2\pi^2)$	tw	2.2839	461	0.478	−256.781 836	3.002
		26	2.315	458	⋯	⋯	⋯
AlBe$^-$	$^3\Pi$ $(7\sigma^1 2\pi^1)$	tw	2.4452	375	0.417	−256.773 224	3.002
		26	2.481	352	⋯	⋯	⋯
AlBe$^-$	$^1\Delta$ $(6\sigma^2 2\pi^2)$	tw	2.3249	435	0.462	−256.766 036	1.0
AlBe$^-$	$^5\Sigma^-$ $(7\sigma^1 6\sigma^1 2\pi^2)$	tw	2.1794	574	0.525	−256.753 241	5.000
AlB	$^3\Sigma^-$ $(6\sigma^2 2\pi^2)$	tw	2.0358	600	0.520	−266.771 273	3.174
		1	2.051	600	⋯	−266.601 94	⋯
		27	2.041	609	⋯	⋯	⋯
AlB	$^3\Pi$ $(7\sigma^1 2\pi^1)$	tw	2.2046	503	0.444	−266.771 225	3.001
		1	2.237	482	⋯	−266.605 85	⋯
AlB	$^1\Delta$ $(6\sigma^2 2\pi^2)$	tw	2.0779	546	0.499	−266.750 108	1.0
		27	2.098	540	⋯	⋯	⋯
AlB	$^5\Sigma^-$ $(7\sigma^1 6\sigma^1 2\pi^2)$	tw	1.9342	780	0.576	−266.734 941	5.000
		1	1.943	792	⋯	−266.552 21	⋯
AlB$^-$	$^4\Sigma^-$ $(7\sigma^1 2\pi^2)$	tw	2.0695	770	0.503	−266.834 266	4.001
AlB$^-$	$^2\Pi$ $(6\sigma^2 2\pi^3)$	tw	1.9974	636	0.540	−266.811 937	2.001
AlB$^-$	$^6\Sigma^-$ $(8\sigma^1 7\sigma^1 6\sigma^1 2\pi^2)^a$	tw	1.9469	noncalc.	0.530	−266.709 956	6.000
AlC	$^4\Sigma^-$ $(7\sigma^1 2\pi^2)$	tw	1.9544	658	0.531	−280.014 465	4.000
		Exp. 53	1.9550	655	0.531	⋯	⋯
		28	1.978	629	⋯	⋯	⋯
AlC	$^2\Pi$ $(6\sigma^2 2\pi^3)$	tw	1.8257	777	0.609	−279.974 469	1.998
		28	1.861	659	⋯	⋯	⋯
AlC	$^4\Pi$ $(7\sigma^1 6\sigma^1 2\pi^3)$	tw	1.7779	1007	0.642	−279.929 206	3.999
		28	1.824	799	⋯	⋯	⋯
AlC$^-$	$^3\Pi$ $(7\sigma^1 2\pi^3)$	tw	1.8708	747	0.580	−280.054 044	3.157
AlC$^-$	$^3\Sigma^+$ $(7\sigma^2 2\pi^2)$	tw	1.9363	701	0.541	−280.046 892	3.003
AlC$^-$	$^1\Sigma^+$ $(6\sigma^2 2\pi^4)$	tw	1.7961	835	0.629	−280.036 378	1.0
AlN	$^3\Pi$ $(7\sigma^1 2\pi^3)$	tw	1.7909	756	0.570	−296.721 178	3.010
		30	1.814	746	⋯	⋯	⋯
AlN	$^3\Sigma^-$ $(7\sigma^2 2\pi^2)$	tw	1.9156	628	0.498	−296.721 272	3.002
		30	1.909	637	⋯	⋯	⋯
AlN	$^1\Sigma^+$ $(6\sigma^2 2\pi^4)$	tw	1.6667	985	0.658	−296.705 968	1.0
		30	1.693	919	⋯	⋯	⋯
AlN	$^3\Sigma^+$ $(7\sigma^1 6\sigma^1 2\pi^4)$	tw	1.6366	1070	0.683	−296.652 871	3.009
		30	1.678	905	⋯	⋯	⋯
AlN$^-$	$^2\Sigma^+$ $(7\sigma^1 2\pi^4)$	tw	1.7056	920	0.630	−296.791 461	2.123
AlN$^-$	$^2\Pi$ $(7\sigma^2 2\pi^3)$	tw	1.7727	827	0.582	−296.787 976	2.141

TABLE I. *(Continued.)*

Species	State	Ref.	R_e	ω_e	B_e	E_{tot}	$\langle 2S+1 \rangle$
AlN$^-$	$^4\Pi$ $(8\sigma^1 7\sigma^1 2\pi^3)$[a]	tw	1.8012	719	0.564	−296.695 861	4.001
AlN$^-$	$^4\Sigma^-$ $(8\sigma^1 2\pi^2)$[a]	tw	1.9385	569	0.488	−296.692 445	4.001
AlO	$^2\Sigma^+$ $(7\sigma^1 2\pi^4)$	tw	1.6241	957	0.637	−317.291 511	2.007
		32	1.638	972	0.641	−317.035 06	⋯
		37	1.6711	915	⋯	⋯	⋯
		Exp. 50	1.6176	978	0.641	⋯	⋯
AlO	$^2\Pi$ $(7\sigma^2 2\pi^3)$	tw	1.7709	733	0.535	−317.271 545	2.001
		37	1.8516	674	⋯	⋯	⋯
AlO	$^4\Sigma^-$ $(7\sigma^1 2\pi^3 3\pi^1)$	tw	1.7730	732	0.534	−317.163 291	4.001
AlO$^-$	$^1\Sigma^+$ $(7\sigma^2 2\pi^4)$	tw	1.6433	969	0.622	−317.388 973	1.0
		38	1.6450	945	⋯	−317.151 90	⋯
		39	1.6586	936	⋯	−317.142 21	⋯
		40	1.6393	965	⋯	⋯	⋯
AlO$^-$	$^3\Pi$ $(7\sigma^1 3\pi^1)$	tw	1.6477	978	0.618	−317.294 233	3.002
AlO$^-$	$^3\Pi$ $(8\sigma^1 2\pi^3)$[a]	tw	1.7862	677	0.526	−316.242 715	3.001
AlF	$^1\Sigma^+$ $(7\sigma^2 2\pi^4)$	tw	1.6596	803	0.549	−342.017 821	1.0
		41	1.664	805	0.546	−341.734 090	⋯
		42	1.6544	800	0.5595	−341.717 14	⋯
		43	1.6680	805	⋯	−341.805 46	⋯
		3	1.6995	764	⋯	−341.662 030	⋯
		Exp.[b]	1.6544	803	⋯	⋯	⋯
AlF	$^3\Pi$ $(7\sigma^1 3\pi^1)$	tw	1.6528	830	0.553	−341.894 986	3.000
		42	1.6922	795	⋯	−341.539 757	⋯
		Exp.[b]	1.6476	828	⋯	⋯	⋯
AlF$^-$	$^2\Pi$ $(7\sigma^2 3\pi^1)$	tw	1.7001	696	0.523	−342.011 568	2.000
AlF$^-$	$^4\Sigma^-$ $(7\sigma^1 3\pi^2)$	tw	1.6969	724	0.525	−341.919 838	4.000
		3	1.7475	978	⋯	−341.558 117	⋯
AlF$^-$	$^4\Pi$ $(8\sigma^1 7\sigma^1 3\pi^1)$[a]	tw	1.6683	noncalc.	0.543	−341.872 719	4.000

[a]Nonbound also in the Koopmans' sense, i.e., the anion highest orbital molecular orbital (HOMO) has a positive eigenvalue.
[b]See References in Ref. 3.

second excited state, which is stable with respect to the decay to the AlBe (ground state)+e decay.

The bottom panel of Table II presents the A_{ad} s computed for the lowest excited states of AlX. As is seen, all the excited AlX species except for AlN can attach an extra electron and form metastable anionic states that should be relatively long lived because their decay to lower neutral states is prohibited by symmetry. It can be expected that some higher excited neutral states are also capable of attaching an extra electron and forming higher metastable anionic states whose decay to lower neutral excited and ground states is prohibited by symmetry. AlF is unstable toward the attachment of an extra electron by 0.17 eV at the CCSD(T)/WMR level.

C. Dissociation energies

Experimental dissociation energies available for AlH and AlF are in good accord with our values (see Table III). For other AlX s, there are theoretical estimates obtained at different levels of theory, many of which are close to our values. There are no experimental data on dissociation energies of the AlX$^-$ anions, and only theoretical estimates are available (for AlH$^-$, AlLi$^-$, AlBe, and AlO$^-$). They are in rather good agreement with our values except for AlO$^-$, where the difference is 0.5 eV. Taking into account the good agreement between our values and the most reliable esti-

mates obtained for other species, we estimate the dissociation energy of AlO$^-$ toward Al+O$^-$ to be 6.4 eV.

All the anions except for AlF$^-$ are stable toward dissociation, and many of them (AlLi$^-$, AlBe$^-$, AlB$^-$, AlN$^-$, and AlO$^-$) are thermodynamically more stable than their neutral parents. The most stable is AlO$^-$, whose dissociation energy of about 150 kcal/mol is higher than dissociation energies of many neutral compounds, including all the neutral AlX species except for AlF, which actually is isoelectronic to AlO$^-$.

D. First-order properties

Table IV presents the results of our calculations of some first-order properties (electric dipole, quadrupole, and octopole moments) for the ground-state AlX species and compares them to the results of other computations. The HF values are obtained at the geometries optimized at the CCSD(T)/WMR level and presented in Table IV to assess the influence of the electron correlation on the first-order properties of AlX. The most significant change, when going from the HF values to the CCSD(T) ones, are observed for AlO, whose CCSD(T) dipole moment is almost twice as large as its HF, dipole moment.

For the closed-shell molecules AlH and AlF, different methods provide dipole moments that are rather close to our

TABLE II. Electron affinities of the second row atoms X and the corresponding diatomic molecules AlX relative to their ground states. All values are in eV.

Level	H	Li	Be	B	C	N	O	F	Al
HF	−0.334	−0.125	−0.526	−0.304	0.451	−1.545	−0.575	1.175	0.010
CCSD(T)[a]	⋯	0.615	⋯	0.238	1.226	⋯	1.338	3.314	⋯
CCSD(T)	0.723	0.616	−0.364	0.242	1.232	−0.259	1.355	3.326	0.406
CCSDT	0.723	0.617	−0.349	0.257	1.240	−0.213	1.361	3.317	0.418
Exp.[b]	0.754	0.618	<0.0	0.277	1.263	<0.0	1.461	3.399	0.441

	AlH	AlLi	AlBe	AlB	AlC		AlN	AlO	AlF
				A_{ad} relative to ground parent states					
Neutral g.s.	$^1\Sigma^+$	$^1\Sigma^+$	$^2\Pi$	$^3\Sigma^-$	$^4\Sigma^-$		$^3\Pi$	$^2\Sigma^+$	$^1\Sigma^+$
Anion g.s.	$^2\Pi$	$^2\Pi$	$^3\Sigma^-$	$^4\Sigma^-$	$^3\Pi$		$^2\Sigma^+$	$^1\Sigma^+$	$^2\Pi$
HF	−1.148	0.143	0.517	1.044	0.013		0.327	1.548	−0.434
CCSD(T)	0.152	0.653	1.131	1.714	1.077		1.912	2.652	−0.170
Other	0.03[c]	0.62[e]	1.09[f]	⋯	⋯		⋯	3.08[g],2.60[h]	⋯
Other	0.04[d]	⋯	⋯	⋯	⋯		⋯	⋯	⋯
Excited anionic states[i]									
CCSD(T)	⋯	⋯	0.90($^1\Delta$),	1.11($^2\Pi$)	0.88($^3\Sigma^+$)		1.82($^3\Pi$)	0.07($^3\Pi$)	⋯
CCSD(T)	⋯	⋯	0.71($^3\Pi$)	⋯	⋯		⋯	⋯	⋯
				A_{ad} relative to excited parent states					
Neutral e. s.	$^3\Pi$	$^3\Pi$	$^4\Sigma^-$	$^1\Delta$	$^2\Pi$		$^3\Sigma^-$	$^2\Pi$	$^3\Pi$
Anion e. s.	$^4\Sigma^-$	$^4\Sigma^-$	$^5\Sigma^-$	$^2\Pi$	$^1\Sigma^+$		⋯	$^3\Pi$	$^4\Sigma^-$
CCSD(T)	0.76	0.68	1.45	1.68	1.68		⋯	0.62	0.68

[a]ANO basis ([$14s9p4d3f/5s4p3d2f$], see Ref. 72).
[b]See Ref. 73. The EA of Al from Ref. 74.
[c]See Ref. 22.
[d]See Ref. 23.
[e]See Ref. 25.
[f]See Ref. 26.
[g]See Ref. 38.
[h]Experimental, see Refs. 55 and 56.
[i]Relative to the ground states of neutral parents; the anion states are in parentheses.

HF or CCSD(T) values; that is, the computed dipole moments of these molecules are insensitive to the level of calculations. The only known experimental first-order property for the AlX species is the dipole moment of AlF, and our computed CCSD(T) value of 1.486 D compares well with the experimental value of 1.5±0.1 D.[80] AlLi, AlN, and AlO possess rather large dipole moments that should be sufficient to sustain dipole-bound states of AlLi⁻, AlN⁻, and AlO⁻ upon detachment of an extra low-energy electron, since dipole moments of ≈2.5 D are required[81,82] for formation of such states.

We have also calculated electric quadrupole ($\Theta_{\alpha\beta}$) and octopole ($\Theta_{\alpha\beta\gamma}$) moments of the AlX series. For linear molecules, both tensors are diagonal and related by $\Sigma_\alpha \Theta_{\alpha\alpha} = 0$ and $\Sigma_\alpha \Theta_{\alpha\alpha\alpha} = 0$. In addition, relations $\Theta_{xx} = \Theta_{yy} = -2\Theta_{zz}$ and $\Theta_{xxz} = \Theta_{yyz} = -2\Theta_{zzz}$ are fulfilled for Σ states.[83] The Π states of AlBe and AlN have different components. Table IV presents our values computed at both HF and CCSD(T) levels. The only theoretical estimate previously obtained for Θ_{zz} of AlH is −5.203 a.u. at the complete active space self-consistent field (CASSCF) level[13] and is in good accord with our CCSD(T) value of −5.778 a.u.

IV. CONCLUSIONS

The results of our CCSD(T)/WMR calculations on the structure of ground and excited states of AlH, AlLi, AlBe, AlB, AlC, AlN, AlO, AlF and their anions suggest the following:

(i)   The ground states of the AlX⁻ anions are the same as the ground states of their isoelectronic AlX species. This allows one to conclude that the periodicity along the rows and columns of the ground states in the sp anions is similar to that of neutral diatomic sp molecules.

(ii)   All of the ground-state AlX species except for AlF can attach an additional electron and form conventional (valence) ground-state anions. The anions AlB⁻, AlC⁻, AlN⁻, and AlO⁻ also possess an excited state, whose total energies are lower than those of the corresponding ground-state parent states. AlBe⁻ has two excited states.

(iii)   The lowest excited states of all the AlX species except for AlN can attach an extra electron and form anionic states that are stable with respect to their neutral par-

TABLE III. Dissociation energies of the ground-state AlX and AlX$^-$ species calculated at the CCSD(T)/WMR level together with experimental and other theoretical data. All values are in eV.

	Neutrals			Anions		
Channel	tw[a]	Other	Channel	tw[a]	Other
AlH ($^1\Sigma^+$)$\rightarrow$Al+H	3.19	3.16$\pm$0.01[b]	AlH$^-$ ($^2\Pi$)$\rightarrow$Al+H$^-$	2.62	2.36[c]
			$\rightarrow$Al$^-$+H	2.94	2.7[d]
AlLi ($^1\Sigma^+$)$\rightarrow$Al+Li	1.06	1.01[e]	AlLi$^-$ ($^2\Pi$)$\rightarrow$Al+Li$^-$	1.09	
			$\rightarrow$Al$^-$+Li	1.30	1.35[e]
AlBe ($^2\Pi$)$\rightarrow$Al+Be	0.59	0.57[f]	AlBe$^-$ ($^3\Pi$)$\rightarrow$Al$^-$+Be	1.32	1.36[f]
AlB ($^3\Sigma^-$)$\rightarrow$Al+B	1.87	1.78[g];	AlB$^-$ ($^4\Sigma^-$)$\rightarrow$Al$^-$+B	3.17	
		1.94[h]	$\rightarrow$Al+B$^-$	3.34	
AlC ($^4\Sigma^-$)$\rightarrow$Al+C	3.41	3.3[i]	AlC$^-$ ($^3\Pi$)$\rightarrow$Al+C$^-$	3.26	
			$\rightarrow$Al$^-$+C	4.08	
AlN ($^3\Pi$)$\rightarrow$Al+N	2.45	2.35;[j] 2.42[k]	AlN$^-$ ($^2\Sigma^+$)$\rightarrow$Al$^-$+N	3.96	
AlO ($^2\Sigma^+$)$\rightarrow$Al+O	5.12	5.25;[l]	AlO$^-$ ($^1\Sigma^+$)$\rightarrow$Al+O$^-$	6.42	6.93[n]
		4.12[m]	$\rightarrow$Al$^-$+O	7.37	
AlF ($^1\Sigma^+$)$\rightarrow$Al+F	7.01	6.89$\pm$0.13,[o]	AlF$^-$ ($^1\Sigma^+$)$\rightarrow$Al+F+e	-0.17	
		6.95,[p] 7.08[q]			

[a]This work.
[b]Experimental, see Ref. 79.
[c]See Ref. 22.
[d]See Ref. 23.
[e]See Ref. 25.
[f]See Ref. 26.
[g]See Ref. 1.
[h]See Ref. 27.
[i]See Ref. 28.
[j]See Ref. 30.
[k]See Ref. 31.
[l]Experimental, see Ref. 57.
[m]See Ref. 31.
[n]See Ref. 38.
[o]Experimental, see Ref. 54.
[p]See Ref. 43.
[q]See Ref. 46.

TABLE IV. Dipole moments (μ, in D), electric quadruple (Θ_{zz}), and octopole (Θ_{zzz}) moments (in atomic units, 1 a.u.=1.345 035 10^{-26} esu) of the ground-state AlX species calculated at the HF and CCSD(T) levels with the WMR basis.

Species	AlH	AlLi	AlBe	AlB	AlC	AlN		AlO	AlF
State	$^1\Sigma^{+a}$	$^1\Sigma^+$	$^2\Pi^b$	$^3\Sigma^-$	$^4\Sigma^-$	$^3\Pi^c$	$^3\Sigma^-$	$^2\Sigma^+$	$^1\Sigma^+$
				HF first-order properties					
μ	-0.133	-3.998	-0.880	2.345	0.938	1.496	1.530	2.284	1.357
Θ_{zz}	-5.913	1.712	2.360	-0.237	-4.616	-3.068	-7.612	-2.819	-4.674
Θ_{zzz}	11.073	-72.434	-17.290	-18.763	-5.831	-7.763	5.920	-8.114	-4.719
				CCSD(T) first-order properties					
μ	0.033[d]	-2.971	-0.119	1.785	1.756[f]	2.636	1.606	4.427[g]	1.486[h]
Θ_{zz}	-5.778[e]	1.866	1.326	1.265	-3.641	-2.297	-6.488	-2.162	-3.766
Θ_{zzz}	12.987	-61.242	-9.957	-12.189	-1.628	-3.732	6.657	-4.433	-3.115

[a]HF/WMR results: R_e=1.6457, B_e=6.406, μ=-0.108, Θ_{zz}=-5.933, Θ_{zzz}=11.138.
[b]HF components are Θ_{xx}=-5.175, Θ_{yy}=2.815, Θ_{yyz}=5.82, Θ_{xxz}=11.46; CCSD(T) components are Θ_{xx}=4.213, Θ_{yy}=2.886, Θ_{yyz}=2.421, Θ_{xxz}=7.536.
[c]HF components are Θ_{xx}=0.114, Θ_{yy}=2.954, Θ_{yyz}=0.271, Θ_{xxz}=7.492; CCSD(T) components are Θ_{xx}=-0.297, Θ_{yy}=2.594, Θ_{yyz}=-1.026, Θ_{xxz}=4.758.
[d]Other (non-HF) theoretical estimates are -0.098 (Ref. 7), -0.119 (Ref. 12), 0.010 (Ref. 13), -0.026 (Ref. 20), 0.012 (Ref. 21).
[e]A theoretical estimate is -5.203 (Ref. 13).
[f]A CASSCF value is 1.0 (Ref. 28).
[g]From 4.2 to 5.2 at different levels (Ref. 32).
[h]Experimental value is 1.5$\pm$0.1; theoretical estimates are 1.543 (Ref. 41), 1.425 (Ref. 45), 1.15 (Ref. 49).

ents. These excited anionic states could have appreciable lifetimes because their decay is prohibited by symmetry.

(iv) All the ground-state anions are thermodynamically rather stable. Some of them, namely: $AlLi^-$, $AlBe^-$, AlB^-, AlN^-, and AlO^- are more stable than their neutral parents. The ''champion'' is AlO^-, whose dissociation energy of 6.42 eV exceeds bond-rupture energies of many neutral chemical compounds.

(v) The dipole moments of AlLi, AlN, and AlO are sufficiently large (>2.5 D) that they should possess dipole-bound anion states.

ACKNOWLEDGMENTS

[1] A. I. Boldyrev, N. Gonzales, and J. Simons, J. Phys. Chem. **98**, 9931 (1994).
[2] A. I. Boldyrev and J. Simons, *Periodic Table of Diatomic Molecules* (Wiley, London, 1997).
[3] G. Gutsev, A. Leś, and L. Adamowicz, J. Chem. Phys. **100**, 8925 (1994).
[4] T. Pluta, R. J. Bartlett, and L. Adamowicz, Phys. Rev. A **40**, 2253 (1989).
[5] F. Luo, G. C. McBane, G. Kim, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **98**, 3564 (1993).
[6] P. J. Bruna and F. Grein, J. Phys. B **22**, 1913 (1989).
[7] W. Meyer and P. Rosmus, J. Chem. Phys. **63**, 2356 (1975).
[8] R. J. Bartlett and D. M. Silver, J. Chem. Phys. **64**, 4578 (1976).
[9] H. Stoll, C. M. E. Pavlidou, and H. Preuss, Theor. Chim. Acta **149**, 143 (1978).
[10] M. F. Guest and S. Wilson, Chem. Phys. Lett. **72**, 49 (1980).
[11] J. A. Pople, M. J. Frisch, and J. S. Binkley, J. Phys. Chem. **89**, 2198 (1985).
[12] J. M. O. Matos, P-Å. Malmqvist, and B. O. Roos, J. Chem. Phys. **86**, 5032 (1987).
[13] J. M. O. Matos, B. O. Roos, and A. J. Sadley, Chem. Phys. **119**, 71 (1988).
[14] V. J. Barclay and J. S. Wright, Chem. Phys. **121**, 381 (1988).
[15] C. W. Baushlicher, Jr. and S. R. Langhoff, J. Chem. Phys. **89**, 2116 (1988).
[16] M. Wilson, M. B. Coolidge, and G. J. Mains, J. Phys. Chem. **96**, 4851 (1992).
[17] S. Koseki, M. W. Schmidt, and M. S. Gordon, J. Phys. Chem. **96**, 10768 (1992).
[18] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **99**, 1914 (1993).
[19] P. Schwerdtfeger and J. Ischtwan, J. Mol. Struct.: THEOCHEM **306**, 9 (1994).
[20] R. J. Cave, J. L. Johnson, and M. A. Anderson, Int. J. Quantum Chem. **50**, 135 (1994).
[21] P. Pullumbi, C. Mijoule, L. Manceron, and Y. Bouteiller, Chem. Phys. **185**, 13 (1994).
[22] P. Rosmus and W. Meyer, J. Chem. Phys. **69**, 2745 (1978).
[23] J. A. Pople, P. v. R. Schleyer, J. Kaneti, and G. W. Spitznagel, Chem. Phys. Lett. **145**, 359 (1988).
[24] M. Nooijen and R. J. Bartlett, J. Chem. Phys. **102**, 3629 (1995).
[25] A. I. Boldyrev, J. Simons, and P. v. R. Schleyer, J. Chem. Phys. **99**, 8793 (1993).
[26] C. W. Baushlicher, Jr., S. R. Langhoff, and H. Patridge, J. Chem. Phys. **96**, 1240 (1992).
[27] C. W. Bauschlicher, Jr. and S. R. Langhoff, J. Chem. Phys. **101**, 80 (1994).
[28] C. W. Baushlicher, Jr., S. R. Langhoff, and L. G. M. Pettersson, J. Chem. Phys. **89**, 5747 (1988).
[29] A. V. Zaitsevskii, A. I. Dement'ev, and G. N. Zviasadze, J. Less-Common Met. **117**, 237 (1986).
[30] S. R. Langhoff, C. W. Baushlicher, Jr., and L. G. M. Pettersson, J. Chem. Phys. **89**, 7354 (1988).
[31] M. Pelissier and J. P. Malrieu, J. Mol. Spectrosc. **77**, 322 (1978).
[32] B. H. Lengsfield III and B. Liu, J. Chem. Phys. **77**, 6083 (1982).
[33] G. W. Spitznagel, T. Clark, P. v. R. Schleyer, and W. J. Hehre, J. Comput. Chem. **8**, 1116 (1987).
[34] U. Meier and V. Staemmler, Theor. Chim. Acta **76**, 95 (1989).
[35] A. I. Boldyrev and P. v. R. Schleyer, J. Am. Chem. Soc. **113**, 9045 (1991).
[36] S. Sakai, J. Phys. Chem. **96**, 131 (1992).
[37] A. Márquez, M. J. Capitán, J. A. Odriozola, and J. F. Sanz, Int. J. Quantum Chem. **52**, 1329 (1994).
[38] K. A. Peterson and R. C. Woods, J. Chem. Phys. **90**, 7239 (1989).
[39] K. A. Peterson and R. C. Woods, J. Chem. Phys. **92**, 6061 (1990).
[40] K. A. Peterson and R. C. Woods, J. Chem. Phys. **95**, 3528 (1991).
[41] R. Klein and P. Rosmus, Theor. Chim. Acta **66**, 21 (1984).
[42] D. M. Hirst, J. Mol. Spectrosc. **121**, 189 (1987).
[43] K. A. Peterson and R. C. Woods, J. Chem. Phys. **89**, 4929 (1988).
[44] R. S. Langhoff, C. W. Bauschlicher, Jr., and P. R. Taylor, J. Chem. Phys. **88**, 5715 (1988).
[45] K. A. Peterson and R. C. Woods, J. Chem. Phys. **92**, 6061 (1990).
[46] M. W. Wong and L. Radom, J. Phys. Chem. **94**, 638 (1990).
[47] W. Wilson, M. B. Coolidge, and G. J. Mains, J. Phys. Chem. **96**, 4851 (1992).
[48] P. Schwerdtfeger, G. A. Heath, M. Dolg, and M. A. Bennett, J. Am. Chem. Soc. **114**, 7518 (1992).
[49] S. Huzinaga, E. Miyoshi, and M. Sekiya, J. Comput. Chem. **14**, 1440 (1993).
[50] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand–Reinhold, New York, 1979).
[51] E. Ishitani, S. Yoshimoto, H. Higashide, M. Kotoyashi, H. Shinohara, and H. Sato, Chem. Lett. 1203 (1993).
[52] L. R. Brock, J. S. Pilgrim, and M. A. Duncan, Chem. Phys. Lett. **230**, 93 (1994).
[53] C. R. Brazier, J. Chem. Phys. **98**, 2790 (1993).
[54] E. Murad, D. L. Hindenbrand, and R. P. Main, J. Chem. Phys. **45**, 263 (1966).
[55] S. R. Desai, H. Wu, and L.-S. Wang, Int. J. Mass Spectrom. Ion Processes **159**, 75 (1996).
[56] S. R. Desai, H. Wu, C. M. Rohlfing, and L.-S. Wang, J. Chem. Phys. **106**, 1309 (1997).
[57] J. B. Pedley and E. Marshall, J. Phys. Chem. Ref. Data **12**, 967 (1983).
[58] ACES II is a program product of the Quantum Theory Project, University of Florida. J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balkova, D. E. Bernholdt, K.-K. Baeck, P. Rozyczko, H. Sekino, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almlöf and P. R. Taylor), VPROPS (P. R. Taylor), and ABACUS (H. J. Helgaker, Aa. Jensen, P. Jǿrgensen, and P. R. Taylor).
[59] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).
[60] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987).
[61] P. O. Widmark, P.-Å. Malmqvist, and B. O. Roos, Theor. Chim. Acta **77**, 291 (1990).
[62] R. J. Bartlett and J. F. Stanton, *Reviews in Computational Chemistry Vol. V*, edited by K. B. Lipkowit and D. B. Boyd (VCH, Inc., New York, 1994), p. 65.
[63] R. J. Bartlett, in *Modern Electronic Structure Theory*, Part II, edited by D. R. Yarkony (World Scientific Publishing, Singapore, 1995).
[64] M. Medved, M. Urban, and J. Noga, Theor. Chem. Acc. **98**, 75 (1997).
[65] S. A. Perera, J. D. Watts, and R. J. Bartlett, J. Chem. Phys. **100**, 1425 (1994).
[66] G. D. Purvis III, H. Sekino, and R. J. Bartlett, Collect. Czech. Chem. Commun. **53**, 2203 (1988).
[67] J. E. Kouba and Y. Öhrn, J. Chem. Phys. **53**, 3246 (1970).
[68] A. V. Zaitsevskii, A. I. Dement'ev, and G. N. Zviadadze, Russ. J. Phys. Chem. **59**, 1392 (1985).
[69] A. I. Boldyrev and J. Simons, J. Phys. Chem. **97**, 1526 (1993).
[70] A. I. Boldyrev and J. Simons, J. Phys. Chem. **97**, 6149 (1993).
[71] J. Kalcher and A. F. Sax, Chem. Rev. **94**, 2291 (1994).
[72] M. Urban, R. J. Bartlett, and S. A. Alexander, Int. J. Quantum Chem. **S26**, 271 (1992).
[73] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).
[74] D. Calabrese, A. M. Covington, and J. S. Thompson, Phys. Rev. A **54**, 2797 (1996).

[75] G. L. Gutsev and R. J. Bartlett, Chem. Phys. Lett. **265**, 12 (1997).

[76] G. L. Gutsev, P. Jena, and R. J. Bartlett, Chem. Phys. Lett. **291**, 547 (1998).

[77] G. L. Gutsev and R. J. Bartlett, J. Chem. Phys. **105**, 8785 (1996).

[78] G. L. Gutsev, P. B. Rozyczko, R. J. Bartlett, and C. A. Weatherford, J. Chem. Phys. (in press).

[79] P. Baltayan and O. Nedelec, J. Chem. Phys. **70**, 2399 (1979).

[80] D. R. Lide, J. Chem. Phys. **42**, 1013 (1965).

[81] G. L. Gutsev and L. Adamowicz, J. Phys. Chem. **99**, 13412 (1995).

[82] C. Desfrançois, H. Abdoul-Carime, and J. P. Schermann, Int. J. Mod. Phys. B **10**, 1339 (1996).

[83] A. D. Buckingham, Quart. Rev. **13**, 183 (1959).