Ab Initio Ground-State Potential Energy Function and Vibration-Rotation Energy Levels of Aluminum Monohydride

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The accurate ground-state potential energy function of aluminum monohydride (AlH) has been determined from ab initio calculations using the multireference averaged coupled-pair functional (MR-ACPF) method in conjunction with the correlation-consistent core-valence basis sets up to septuple-zeta quality. The vibration-rotation energy levels of the two isotopologues, AlH and AlD, were predicted to near the "spectroscopic" accuracy. The importance of electron correlation beyond the MR-ACPF level of approximation, the scalar relativistic, spin-orbit, adiabatic, and nonadiabatic effects was discussed. © 2019 Wiley Periodicals, Inc.

Introduction

Aluminum monohydride (AlH) is one of the simplest metallic hydrides, consisting of only 2 nuclei and 14 electrons. It was the subject of numerous theoretical studies, see for example Refs. [1–11], and this list is by no means exhaustive. Because the AlH molecule served as an attractive benchmark system, its electronic structure in the ground and excited electronic states was characterized at various levels of theory. In the most extensive study to date by Wells and Lane,[9] the potential energy functions for several electronic states of AlH were determined using the multireference valence configuration interaction approach with large correlation-consistent basis sets, MRCI+Q/aug-cc-pV6Z. Despite the high level of theory applied in that work, the experimental vibrational term values for the ground electronic state of AlH, $X\ ^1\Sigma^+$, were rather poorly reproduced. Differences between the experimental and calculated vibrational term values ranged from 18 cm^{-1} ($v = 0$) to 155 cm^{-1} ($v = 3$), where v is the vibrational quantum number. The small active space used by Wells and Lane[9] to construct the reference space for the MRCI calculation is the most likely reason for such a large discrepancy between theory and experiment. The spectroscopic constants for the $X\ ^1\Sigma^+$ state of AlH, obtained using the single-reference coupled-cluster approach with large correlation-consistent basis sets, were recently reported by Ferrante et al. [11] The potential energy function near the equilibrium configuration (for the AlH internuclear distance of 1.2–2.2 Å) was calculated up to the valence CCSDTQ/aug-cc-pVQZ level of theory. Corrections for the core-electron correlation, relativistic, and adiabatic effects were additionally included. The vibrational fundamental wavenumbers v for the AlH and AlD isotopologues were predicted to be 1632 and 1185 cm^{-1},[11] respectively, compared with the corresponding experimental values of 1625 and 1182 cm^{-1}.[12]

The vibration-rotation spectra of AlH and AlD attracted also significant interest by various experimentalists, see Refs. [12–25] and references therein. The vibration-rotation energy levels of the $X\ ^1\Sigma^+$ state of AlH and AlD were characterized by high-resolution spectroscopy up to the seventh excited vibrational state. For a summary of previous spectroscopic work on AlH, the reader is referred to the recent study by Yurchenko et al. [25]

The aim of this work is to provide the accurate state-of-the-art potential energy function for the ground electronic state of AlH and to discuss the effects, which should be taken into account in order to predict the vibration-rotation energy levels of AlH to near the "spectroscopic" accuracy. In computational chemistry, such an accuracy means error bars on the predicted vibrational fundamental wavenumbers smaller than ± 1 cm^{-1} and those on the predicted equilibrium internuclear distances smaller than about ± 0.0001 Å. As shown in this work, the "spectroscopic" accuracy for AlH can only be achieved by applying large basis sets, close to the complete-basis-set limit, and accounting for both the core- and valence-electron correlation effects. Additionally, the scalar relativistic, spin-orbit, adiabatic, and nonadiabatic effects should all be taken into consideration.

Methodology

The molecular parameters of AlH were determined using the multireference averaged coupled-pair functional (MR-ACPF) method[26,27] in conjunction with the augmented correlation-consistent core-valence basis sets up to septuple-zeta quality, aug-cc-pCVnZ ($n = 5$–7). The MR-ACPF method is an approximately size-extensive variant of the multireference configuration interaction (MRCI) approach including single and double excitations. The calculations consisted of the complete-active-space self-consistent-field (CASSCF) step followed by the internally contracted[28] MR-ACPF step. The MOLPRO package of ab initio programs was employed.[29] The usual full-valence active space, consisting of the 3s- and 3p-like orbitals of the

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aluminum atom and the 1s-like orbital of the hydrogen atom, was extended with the 4s-, 4p-, and 3d-like orbitals of the aluminum atom. The CASSCF wave function of AlH included thus all excitations of 4 valence electrons in 14 molecular orbitals. As shown by Bauschlicher and Langhoff,[1] the second-order configuration interaction (SOCI) treatment based on this active space gave the predictions of molecular properties of AlH in near perfect agreement with the full configuration interaction (FCI) treatment. In the generation of the CASSCF wave functions, the 1s-, 2s-, and 2p-like core orbitals of the aluminum atom were optimized, but they were kept doubly occupied. The reference function for the MR-ACPF calculation consisted of the CASSCF orbitals, resulting in 881 reference configuration state functions for the $X\ ^1\Sigma^+$ state of AlH. In the MR-ACPF step, all but Al 1s electrons were correlated through single and double excitations. Because of the huge orbital energy gap, the correlation effects of deep-core 1s electrons of aluminum are likely to be negligible.

The one-particle basis sets for aluminum consisted of the valence cc-pV($n + d$)Z basis sets augmented with diffuse (aug) and tight (C) functions. The valence cc-pV($n + d$)Z basis sets up to sextuple-zeta quality were developed by Dunning et al.[30] The largest basis set for aluminum available in the literature, cc-pV(6 + d)Z, contains the primitive (21s14p6d4f3g2h1i) functions contracted to [8s7p6d4f3g2h1i]. The cc-pV(7 + d)Z basis set was developed for this study. This basis set contains the primitive (27s18p7d5f4g3h2i1k) functions contracted to [9s8p7d5f4g3h2i1k]. Because the MOLPRO package cannot handle functions higher than i, the k polarization function was omitted in all subsequent calculations. The diffuse functions for aluminum, up to the basis set of sextuple-zeta quality aug-cc-pV(6 + d)Z, were taken from the literature.[30] For the aug-cc-pV(7 + d)Z basis set, the customary even-tempered exponents were calculated in this work by multiplying the exponent of the outermost primitive function of a given angular symmetry in the valence basis set by a factor of 0.4. To account for the correlation effects of the 2s- and 2p-like core orbitals of the aluminum atom, the basis sets were augmented with tight functions. The largest core-valence basis set of sextuple-zeta quality for aluminum, cc-pCV6Z, available in the literature,[31,32] was obtained by augmenting the cc-pV6Z basis set with the primitive (5d4f3g2h1i) functions and contracting the primitive (21s14p) functions to [12s11p]. In this work, the cc-pV(7 + d)Z basis set was augmented with the primitive (5d5f4g3h2i1k) functions and the primitive (27s18p) functions were contracted to [15s14p]. As for the valence basis set, the k tight function was omitted. The details of this basis set and results of the supporting benchmark calculations will be reported elsewhere. The one-particle basis sets for hydrogen consisted of the valence cc-pVnZ basis sets augmented with diffuse (aug) functions.[33]

The total energy for the aluminum atom in its ground electronic state ^2P was calculated using the MR-ACPF method, with the active space described above and all but Al 1s electrons being correlated, to be −242.258148, −242.262919, and − 242.264625 E_h for the aug-cc-pCV5Z, aug-cc-pCV6Z, and aug-cc-pCV7Z(i) basis set, respectively.

The vibration-rotation energy levels of AlH were calculated using the Numerov-Cooley method.[34] The energy levels were

calculated using the nuclear masses of aluminum and hydrogen (26.974406991, 1.007276452, and 2.013553198 u for ^{27}Al, H, and D, respectively).

Results and Discussion

To determine the shape of the potential energy function of AlH, the total energies were calculated at the MR-ACPF/aug-cc-pCVnZ (n = 5–7) level of theory at 85 internuclear distances ranging from 0.9 to 50 Å. The predicted molecular parameters for the $X\ ^1\Sigma^+$ state of AlH are given in Table 1. The parameters quoted include the equilibrium internuclear distance r_e, the total energy at minimum, the binding energy D_e, the vibrational fundamental wavenumber ν, and the ground-state effective (vibrationally averaged) rotational constant B_0. The equilibrium internuclear distance r_e was determined by fitting the predicted total energies, in the close vicinity of the minimum, with a polynomial expansion. For a given vibrational state, the effective rotational constant B_v was determined, along with the centrifugal distortion constants D_v and H_v, by fitting the predicted rotation energies with a power series in $J(J + 1)$, where J is the rotational quantum number. The predicted values tend clearly to converge with enlargement of the one-particle basis set. Changes in the calculated equilibrium distance r_e and the binding energy D_e beyond the aug-cc-pCV7Z(i) basis set are estimated to be smaller than 0.0002 Å and 10 cm^{-1}, respectively. The analogous changes in the vibrational fundamental wavenumber ν and the effective rotational constant B_0 are estimated to be about 0.3 and 0.001 cm^{-1}, respectively. The potential energy function for the $X\ ^1\Sigma^+$ state of AlH, obtained at the best MR-ACPF/aug-cc-pCV7Z(i) level of theory, is referred further to as "CV".

The effects of electron correlation beyond the MR-ACPF level of approximation were estimated by comparing the total energies of AlH calculated using either FCI or MR-ACPF methods, both with the aug-cc-pV(T + d)Z basis set and only valence electrons being correlated. As expected from work of Bauschlicher and Langhoff,[1] differences between the FCI and MR-ACPF total energies of AlH were found to be very small for all of the internuclear distances under consideration. These differences amount to about 4 μE_h in the vicinity of the equilibrium configuration of AlH and 2 μE_h at the dissociation limit, reaching a maximum of about 12 μE_h at the internuclear

Table 1. Molecular parameters for the $X\ ^1\Sigma^+$ state of AlH determined at the MR-ACPF/aug-cc-pCVnZ level of theory.

	n = 5	n = 6	n = 7
r_e [a] (Å)	1.64588	1.64538	1.64522
$E+242$ [b] (hartree)	−0.875249	−0.880129	−0.881873
D_e [c] (cm^{-1})	25,664	25,687	25,695
ν [d] (cm^{-1})	1626.76	1629.52	1629.81
B_0 [e] (cm^{-1})	6.31466	6.31960	6.32080

[a] The equilibrium internuclear distance.
[b] The total energy at a minimum.
[c] The binding energy.
[d] The vibrational fundamental wavenumber.
[e] The ground-state effective rotational constant.

distance of about 3.4 Å. The CASSCF/MR-ACPF treatment based on the extended active space described above accounts thus for nearly the whole valence correlation energy for the $X\ ^1\Sigma^+$ state of AlH. The differences between the FCI and MR-ACPF total energies were added at each point of the potential energy function CV, yielding the function referred to as "CV + F".

The potential energy function of AlH was further corrected for the scalar relativistic effects using the exact-2-component (X2C) approach.[35] The relativistic contribution to the total energy of AlH was calculated at the MR-ACPF/aug-cc-pV(5 + d)Z (uncontracted) level of theory, only valence electrons being correlated. At each point of the potential energy function of AlH, the scalar relativistic correction was determined as a difference in the total energy calculated using either the X2C or nonrelativistic Hamiltonian. The scalar relativistic effects were found to decrease the total energy of AlH in the $X\ ^1\Sigma^+$ state by about 437 mE_h. The potential energy function corrected in this way is referred to as "CV + F + R".

The AlH molecule in its $X\ ^1\Sigma^+$ state dissociates to give the aluminum atom in its ^2P state and the hydrogen atom in its ^2S state. Therefore, the spin-orbit effects should also be considered. These effects were investigated using the Breit-Pauli spin-orbit operator and the multireference configuration interaction method including the cluster Davidson correction, MRCI+Q.[36] The total energy contributions were calculated with the uncontracted aug-cc-pCVQZ basis set and all but Al 1s electrons being correlated. Four electronic states of AlH, correlating to the Al(^2P) + H(^2S) atomic states at the dissociation limit, were considered simultaneously. These states are $X\ ^1\Sigma^+$, $a\ ^3\Pi$, $A\ ^1\Pi$, and $1\ ^3\Sigma^+$. The spin-orbit effects were found to decrease the total energy of AlH in the $X\ ^1\Sigma^+$ state by less than 2 μE_h for most internuclear distances under consideration, except for those larger than about 3.3 Å. In the vicinity of the equilibrium configuration of AlH, the total energy decrease amounts to just 0.7 μE_h, whereas at the dissociation limit, it is predicted to be 327 μE_h. The spin-orbit splitting at the dissociation limit of AlH is predicted to be 108 cm^{-1}, compared with the corresponding experimental value[37] of 112.061 cm^{-1} for the aluminum atom in its ^2P state. The spin-orbit corrections were added to the potential energy function of AlH. The resulting function, referred to as "CV + F + R + S", is the best estimate of the Born-Oppenheimer potential energy function of AlH in its $X\ ^1\Sigma^+$ state.

To account for the adiabatic effects, the diagonal Born-Oppenheimer correction (DBOC)[38,39] was determined for two isotopologues, AlH and AlD. The restricted-active-space configuration interaction (RAS CI)[40] method was used, with the aug-cc-pCVTZ basis set and only valence electrons being correlated through single and double excitations. The calculations were performed using the PSI3 package of ab initio programs.[41] The active space (RAS2) for the RAS CI wave function of AlH consisted of five molecular valence orbitals, namely the 3s- and 3p-like orbitals of the aluminum atom and the 1s-like orbital of the hydrogen atom. In the vicinity of the equilibrium configuration of AlH, the DBOC was determined to be about 4.59 mE_h. For the AlD isotopologue, the corresponding DBOC was determined to be about 4.39 mE_h. The DBOC values were calculated at the

same set of points as the Born-Oppenheimer potential energy functions discussed above and were subsequently added to the CV + F + R + S total energies. The resulting mass-dependent adiabatic potential energy functions are referred to as "CV + F + R + S + D".

Changes in the total energy for the $X\ ^1\Sigma^+$ state of AlH due to electron correlation beyond the MR-ACPF level of approximation (F), the scalar relativistic effects (R), and the adiabatic effects (D) with the internuclear distance are illustrated in Figure 1. The changes due to the spin-orbit effects are not shown, because this plot is just a horizontal line in the scale of the figure.

For each of the potential energy functions calculated for the $X\ ^1\Sigma^+$ state of AlH, the molecular parameters were determined. The results are given in Table 2. The total corrections F + R + S to r_e, D_e, ν, and B_0 amount to 0.00015 Å, −102, −2.58, and −0.00141 cm^{-1}, respectively. As illustrated by Table 2, these are the scalar relativistic and adiabatic corrections, which affect the predicted molecular parameters of AlH the most. The spin-orbit corrections are negligible, except for the binding energy D_e. The best predicted Born-Oppenheimer potential energy function of AlH (CV + F + R + S) has a minimum at 1.64537 ± 0.00020 Å and the well depth of 25,593 ± 10 cm^{-1}. The predicted equilibrium distance r_e is in perfect agreement with the experimental Born-Oppenheimer estimate of 1.6453622(21) Å by White et al.[12] However, given the (conservative) uncertainty in the ab initio predicted r_e value due to the limited basis set size, such quantitative agreement seems to be somewhat fortuitous. An another experimental estimate of the equilibrium distance r_e of AlH in its $X\ ^1\Sigma^+$ state was reported by Szajna et al.[22] to be 1.64735188(26) Å. The large discrepancy between the two experimental estimates of r_e is quite puzzling at first glance. It results from distinctly different ways of deriving the equilibrium distance r_e in both the experimental studies.[12,22] The later value still includes mass-dependent contributions resulting from the adiabatic and nonadiabatic effects. These effects were explicitly accounted for in work of White et al.[12] Yet
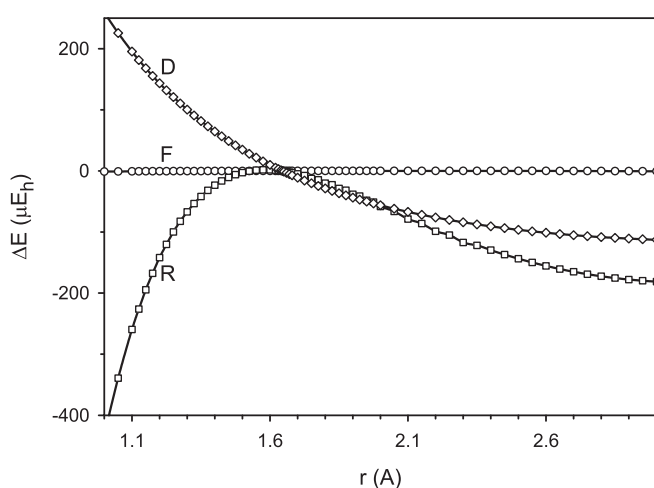
Figure 1. Changes in the total energy ΔE for the $X\ ^1\Sigma^+$ state of AlH due to electron correlation beyond the MR-ACPF level of approximation (F, circles), the scalar relativistic effects (R, squares), and the adiabatic effects (D, diamonds) as functions of the internuclear distance r. The relative values of ΔE are plotted, taking the absolute changes ΔE calculated for r = 1.645 Å as the origin of the ΔE axis.

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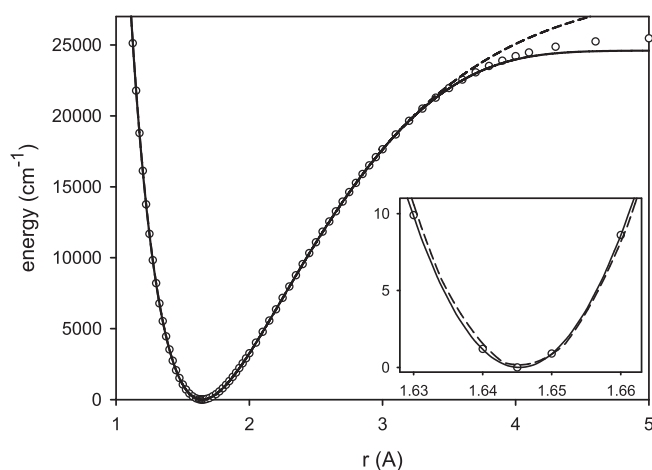| **Table 2.** Molecular parameters[a] for the $X\,^1\Sigma^+$ state of AlH determined using various potential energy functions.					
	CV[b]	CV + F[c]	CV + F + R[c]	CV + F + R + S[c]	CV + F + R + S + D[c]
r_e (Å)	1.64522	1.64521	1.64538	1.64537	1.64594
$E+242$ (hartree)	−0.881873	−0.881869	−1.318627	−1.318628	−1.314033
D_e (cm^{-1})	25,695	25,694	25,665	25,593	25,566
ν (cm^{-1})	1629.81	1629.85	1627.23	1627.23	1626.11
B_0 (cm^{-1})	6.32080	6.32086	6.31938	6.31939	6.31504
[a] See Table 1.					
[b] The potential energy function was calculated at the MR-ACPF/aug-cc-pCV7Z(i) level of theory.					
[c] Including additionally the full-configuration-interaction (F), scalar relativistic (R), spin-orbit (S), and diagonal Born-Oppenheimer (D) corrections (see the text).					

another experimental estimate of r_e = 1.645793 Å was recently derived by Yurchenko et al. [25] from a global analysis of the spectroscopic data of AlH. In that work, only the nonadiabatic effects were explicitly considered and, therefore, the difference r_e(Yurchenko et al.) − r_e(White et al.) of 0.000431 Å is a measure of the adiabatic effects for the $X\,^1\Sigma^+$ state of AlH (see below). Previous best theoretical estimates of the equilibrium distance of AlH in its $X\,^1\Sigma^+$ state were 1.6510 Å by Shi et al.,[7] 1.6454 Å by Karton and Martin,[8] 1.635 Å by Wells and Lane,[9] 1.6465 Å by Brown and Wasylishen,[10] and 1.647 Å by Ferrante et al. [11] The best predicted binding energy D_e for the $X\,^1\Sigma^+$ state of AlH is close to the experimental value of 25,490(80) cm^{-1} derived by Baltayan and Nedelec.[42] For the AlH and AlD isotopologues, the adiabatic equilibrium internuclear distance r_e is predicted in this work to be longer than the Born-Oppenheimer counterpart by 0.00057 and 0.00029 Å, respectively. The adiabatic corrections to the Born-Oppenheimer binding energy D_e are predicted to be −27 and −13 cm^{-1}, respectively.

Relative energies of the predicted Born-Oppenheimer potential energy function for the $X\,^1\Sigma^+$ state of AlH are given in the supplementary material. Figure 2 illustrates this function in comparison to the empirical potential energy functions derived by White et al. [12] and Yurchenko et al. [25] All of these functions are essentially identical (in the scale of the figure), except for large internuclear distances. The binding energy D_e was assumed by White et al. [12] to be 24,600 cm^{-1}, and it was derived by Yurchenko

Figure 2. The predicted Born-Oppenheimer potential energy function (circles) for the $X\,^1\Sigma^+$ state of AlH in comparison to the empirical potential energy functions derived by White et al.[12] (solid line) and by Yurchenko et al.[25] (dashed line). Inset: expanded view near the minimum.

et al. [25] to be 29,390 cm^{-1}. The ab initio value of 25,593 cm^{-1} is predicted in this work to lie in between.

The adiabatic potential energy functions (CV + F + R + S + D) were used to determine vibration-rotation energy levels for the $X\,^1\Sigma^+$ state of the AlH and AlD isotopologues. The calculated vibrational term values T_v and the effective rotational constants B_v and quartic centrifugal distortion constants D_v are given in Table 3. The predicted values are compared with the experimental values reported by White et al. [12] The predicted vibrational fundamental wavenumbers ν of the AlH and AlD isotopologues overestimate the experimental counterparts by 1.0 and 0.5 cm^{-1}, respectively. Differences between the predicted and experimental vibrational term values T_v increase almost linearly with the increasing quantum number v. Thus, it is the vibrational harmonic frequency ω, which is the most affected by error. For the AlH and AlD isotopologues, the predicted effective rotational constants B_v systematically overestimate the experimental values by about 0.014 and 0.004 cm^{-1}, respectively. The experimental quartic centrifugal distortion constants D_v are systematically overestimated by about 0.028 and 0.005 × 10^{-4} cm^{-1}, respectively.

To account for the effects beyond the adiabatic approximation,[43–45] the vibrational and rotational g-factors, g_v and g_r, were determined for the AlH and AlD isotopologues. The g-factors were included by means of second-order perturbational corrections to the vibrational and rotational terms of the effective vibration-rotation Hamiltonian of a diatomic molecule. The reduced nuclear mass μ in the vibrational term was replaced by the effective vibrational reduced mass defined as $\mu_v = \mu/(1+\beta)$, whereas that in the rotational term was replaced by the effective rotational reduced mass defined as $\mu_r = \mu/(1+\alpha)$.[43–45] The parameters β and α are related to the electronic contributions to the vibrational and rotational g-factors, respectively, as follows: $\beta = (m_e/m_p)g_v^{el}$ and $\alpha = (m_e/m_p)g_r^{el}$, where m_e/m_p is the electron–proton mass ratio. The vibrational and rotational g-factors were calculated at various internuclear distances using the CASSCF method with the aug-cc-pV(5 + d)Z basis set and the extended active space consisting of 14 molecular orbitals (described above). For general theoretical and computational details of these calculations, the reader is referred to Refs. [46–48]. The calculations were performed using the DALTON package of ab initio programs.[49] In the vicinity of the equilibrium configuration of the AlH isotopologue, the nonadiabatic parameters α and β were calculated to be about −2.28×10^{-3} and −0.74×10^{-3}, respectively. Changes in the parameters α and β with the internuclear distance r are illustrated in Figure 3.

Table 3. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X\ ^1\Sigma^+$ state of AlH and AlD.
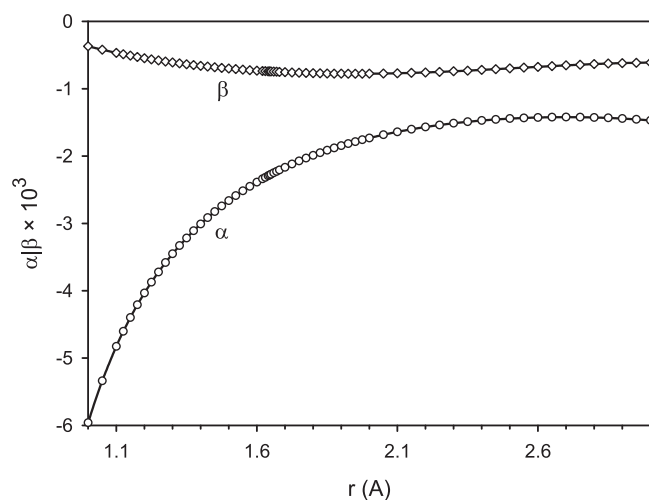
	T_v			B_v			$D_v \times 10^4$		
v	Exp.[a]	Calc.[b]	Δ[c]	Exp.	Calc.	Δ	Exp.	Calc.	Δ
AlH									
0	0.000	0.00		6.300712	6.31504	0.01433	3.65321	3.6817	0.0285
1	1625.070	1626.11	1.04	6.117286	6.13152	0.01423	3.58896	3.6173	0.0283
2	3194.214	3196.38	2.17	5.937438	5.95158	0.01414	3.52508	3.5541	0.0290
3	4708.818	4712.06	3.24	5.761078	5.77496	0.01388	3.46210	3.4910	0.0289
4	6170.194	6174.51	4.32	5.588065	5.60189	0.01383	3.40060	3.4273	0.0267
5	7579.565	7585.08	5.52	5.418219	5.43201	0.01379	3.34124	3.3711	0.0299
6	8938.050	8944.72	6.67	5.251310	5.26495	0.01364	3.28474	3.3075	0.0228
AlD									
0	0.000	0.00		3.283577	3.28728	0.00370	0.98794	0.9917	0.0038
1	1181.943	1182.45	0.51	3.214675	3.21841	0.00373	0.97547	0.9802	0.0047
2	2334.575	2335.66	1.08	3.146743	3.15055	0.00381	0.96302	0.9678	0.0048
3	3458.426	3460.13	1.70	3.079768	3.08358	0.00381	0.95065	0.9555	0.0048
4	4554.010	4556.32	2.31	3.013729	3.01749	0.00376	0.93840	0.9442	0.0058
5	5621.820	5624.65	2.83	2.948602	2.95247	0.00387	0.92635	0.9300	0.0036
6	6662.326	6665.88	3.55	2.884356	2.88826	0.00390	0.91456	0.9202	0.0056

[a] The experimental values determined using the Dunham Y_{ij} constants from Ref. [12].
[b] The values calculated using the adiabatic potential energy function, the zero-point energy is 835.57 and 602.96 cm^{-1} for AlH and AlD, respectively.
[c] A difference between the calculated and experimental values.
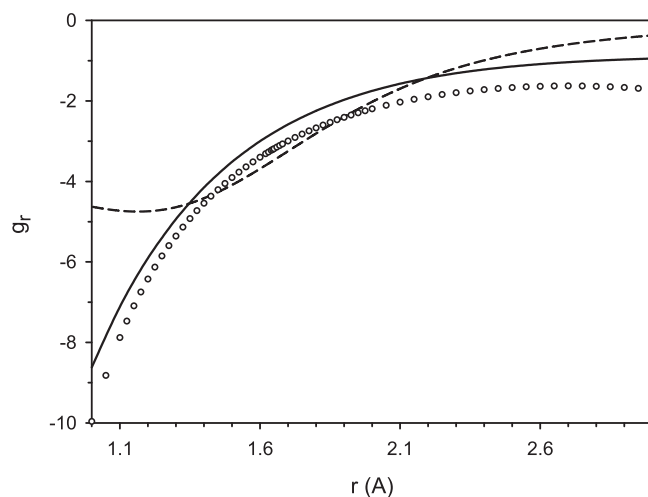
It is interesting to analyze individual second-order perturbational contributions of the excited electronic states of AlH to the nonadiabatic parameters α and β, see eqs. 16 and 17 of Ref. [47]. For the parameter α, the sum over excited states consists of terms including the transition matrix element of the total angular momentum operators $\hat{L}_x$ and $\hat{L}_y$ (with the Al and H nuclei located at the z axis) and the excitation energies. In the vicinity of the equilibrium configuration of AlH, the largest contribution arises from the lowest-energy $^1\Pi$ state A. Contributions from the higher energy $^1\Pi$ states are by the order of magnitude smaller. Over a wide range about the equilibrium configuration of AlH, the sum over excited states is calculated to be nearly constant. Therefore, the dependence of the nonadiabatic parameter α on the internuclear distance r is largely due to the multiplicative factor $1/r^2$. For the parameter β, the sum over excited states consists of terms including the transition matrix

element of the momentum operator $-i\hbar\partial/\partial r$ and the excitation energies. In the vicinity of the equilibrium configuration of AlH, the contribution from the first excited $^1\Sigma^+$ state C amounts to about one-half of the β value. The sum over excited states is predicted to vary slightly with the internuclear distance r, yielding the parameter β to be nearly constant as a function of r.

Figure 4 shows the rotational g-factor $g_r = g_r^{el} + g^{nu}$, as a function of the internuclear distance r, predicted in this work for the $X\ ^1\Sigma^+$ state of AlH. The term g^{nu} is the (constant) nuclear contribution. The ab initio values are compared with the corresponding empirical functions derived by Sauer and Ogilvie[16] and by Yurchenko et al. [25] from analyses of the vibration-rotation spectra of AlH. In the former study, the rotational g-factor at the equilibrium configuration of the AlH

Figure 3. The nonadiabatic parameters α (circles) and β (diamonds) for the $X\ ^1\Sigma^+$ state of AlH as functions of the internuclear distance r.

Figure 4. The rotational g-factor g_r for the $X\ ^1\Sigma^+$ state of AlH as a function of the internuclear distance r. The empirical functions derived by Sauer and Ogilvie[16] (solid line) and by Yurchenko et al. [25] (dashed line) are compared with the ab initio values predicted in this work (circles).

Table 4. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X\ ^1\Sigma^+$ state of AlH and AlD, calculated taking into account the nonadiabatic effects.

v	T_v Calc.[a]	T_v Δ[b]	B_v Calc.	B_v Δ	$D_v \times 10^4$ Calc.	$D_v \times 10^4$ Δ
AlH						
0	0.00		6.30064	−0.00007	3.6520	−0.0012
1	1625.53	0.46	6.11752	0.00023	3.5876	−0.0014
2	3195.25	1.04	5.93799	0.00055	3.5248	−0.0003
3	4710.44	1.62	5.76177	0.00069	3.4621	0.0000
4	6172.42	2.23	5.58910	0.00103	3.3989	−0.0017
5	7582.57	3.00	5.41961	0.00139	3.3432	0.0020
6	8941.83	3.78	5.25295	0.00164	3.2797	−0.0050
AlD						
0	0.00		3.28341	−0.00017	0.9875	−0.0004
1	1182.25	0.31	3.21461	−0.00007	0.9760	0.0005
2	2335.26	0.68	3.14683	0.00009	0.9637	0.0007
3	3459.53	1.10	3.07994	0.00017	0.9514	0.0007
4	4555.54	1.53	3.01393	0.00020	0.9401	0.0017
5	5623.71	1.89	2.94898	0.00038	0.9260	−0.0004
6	6664.78	2.45	2.88486	0.00050	0.9162	0.0016

[a] The calculated values, the zero-point energy is 835.27 and 602.85 cm^{-1} for AlH and AlD, respectively.
[b] A difference between the calculated and experimental values, see Table 3.

molecule was derived to be -2.8 ± 0.5. Using the coupled-cluster singles-and-doubles polarization-propagator approximation (CCSDPPA), Sauer and Ogilvie[16] calculated this parameter to be -3.370. The best Born-Oppenheimer estimate was predicted in this work to be -3.206, lying within the experimental error bars.

The vibrational term values T_v and the effective rotational constants B_v and quartic centrifugal distortion constants D_v calculated for AlH and AlD taking into account the nonadiabatic effects are given in Table 4. A comparison of these spectroscopic parameters with those given in Table 3 shows that the use of the effective vibrational and rotational reduced masses leads to much better agreement with the experimental data. The experimental fundamental wavenumbers ν of the AlH and AlD isotopologues are reproduced to within 0.5 and 0.3 cm^{-1}, respectively. The quoted effective rotational constants B_v of both the isotopologues are reproduced to within 0.00097 and 0.00027 cm^{-1} (the root-mean-square deviation), respectively, whereas the quartic centrifugal distortion constants D_v are reproduced to within 0.0022 and 0.0010 $\times 10^{-4}$ cm^{-1}, respectively. Note that for the ground vibrational state of the AlH and AlD isotopologues, the effective rotational constant B_0 is reproduced to about 0.0001 cm^{-1} on average. It lends credence to the equilibrium AlH bond length r_e predicted in this work. In previous (recent) theoretical work, the constant B_0 for the $X\ ^1\Sigma^+$

state of AlH was predicted to be 6.4027 cm^{-1} [MRCI/aug-cc-pV6Z],[9] 6.319 cm^{-1} [CCSD(T)/cc-pCV5Z],[10] and 6.2963 cm^{-1} [CCSDTQ/aug-cc-pVQZ].[11]

For the ground vibrational state of the AlH and AlD isotopologues, the vibrationally averaged rotational g-factors $\langle g_r \rangle$ were predicted to be -3.163 and -1.646, respectively. Sauer and Ogilvie[16] calculated this parameter for the AlH molecule to be -3.295. The corresponding averaged vibrational g-

Table 5. Vibrationally averaged electric dipole moments $\langle \mu \rangle$ (in D) for the $X\ ^1\Sigma^+$ state of AlH and AlD, calculated using the nonadiabatic vibrational wave functions.

v	AlH	AlD
0	−0.244	−0.218
1	−0.423	−0.346
2	−0.603	−0.476
3	−0.784	−0.606
4	−0.963	−0.736
5	−1.141	−0.865
6	−1.316	−0.994

Table 6. Vibrational term values (T_v) and the effective rotational (B_v) and quartic centrifugal distortion (D_v) constants (in cm^{-1}) for the $X\ ^1\Sigma^+$ state of AlH—all bound vibrational states calculated using the nonadiabatic vibrational wave functions.

v	T_v[a]	B_v	$D_v \times 10^4$
0	0.0	6.3006	3.652
1	1625.5	6.1175	3.588
2	3195.3	5.9380	3.525
3	4710.4	5.7618	3.462
4	6172.4	5.5891	3.399
5	7582.6	5.4196	3.343
6	8941.8	5.2530	3.280
7	10251.4	5.0889	3.237
8	11511.9	4.9271	3.179
9	12724.1	4.7671	3.141
10	13888.6	4.6087	3.109
11	15005.5	4.4504	3.071
12	16075.2	4.2923	3.076
13	17097.1	4.1342	3.060
14	18070.8	3.9726	3.066
15	18995.5	3.8079	3.128
16	19869.7	3.6406	3.172
17	20691.8	3.4637	3.310
18	21457.9	3.2741	3.445
19	22164.5	3.0709	3.794
20	22806.0	2.8531	3.912
21	23379.3	2.6061	4.767
22	23871.9	2.3236	5.225
23	24276.1	1.9848	6.624
24	24573.8	1.5256	11.293
25	24721.3	0.7173	33.771

[a] The zero-point energy is 835.3 cm^{-1}.

factors $\langle g_v \rangle$ were predicted in this work to be -0.382 and -0.166, respectively.

The electric dipole moment of AlH in its $X\ ^1\Sigma^+$ state was determined using the finite field approach. The total energy of the AlH molecule in a static homogeneous electric field was calculated using the MR-ACPF method with the aug-cc-pCV6Z basis set and the extended active space described above. The core-electron correlation and scalar relativistic effects were additionally accounted for. The dipole moment was then calculated using the three-point central difference formula, with the electric field strength of ± 0.001 a.u. At this level of theory, the electric dipole moment of AlH was estimated to be accurate to better than 0.0001 D. The dipole moment function of AlH determined in this way is given in the supplementary material. The electric dipole moment was predicted to be only -0.152 D at the equilibrium configuration of the AlH molecule. This is because the dipole moment function change the sign at the internuclear distance of about 1.6 Å, close to the equilibrium internuclear distance r_e. The natural-bond-orbital atomic net charges in the $X\ ^1\Sigma^+$ state were determined to be about $0.6e$ and $-0.6e$ on the aluminum and hydrogen atoms, respectively. Moreover, the AlH molecule is polarized in this way over a wide range about its equilibrium configuration. Predicted vibrationally averaged electric dipole moments $\langle \mu \rangle$ for the $X\ ^1\Sigma^+$ state of AlH and AlD, calculated using the nonadiabatic vibrational wave functions, are given in Table 5. To our knowledge, the dipole moment of AlH was not determined experimentally so far. For a comparison with the dipole moment estimates in previous theoretical work on AlH, the reader is referred to the study by Brown and Wasylishen.[10]

Finally, the spectroscopic parameters predicted for all bound vibration-rotation energy levels for the $X\ ^1\Sigma^+$ state of AlH are summarized in Table 6. The highest excited vibrational state, $v = 25$, is predicted to lie in energy only 9 cm^{-1} below the dissociation limit. The results reported can assist future experimental detection of highly excited states of AlH by high-resolution vibration-rotation spectroscopy and can be useful for determining partition functions for molecules of astrophysical interest.[50]

Conclusions

In conclusion, the accurate potential energy function of aluminum monohydride and monodeuteride in the ground electronic state $X\ ^1\Sigma^+$ was determined in the state-of-the-art ab initio calculations. The vibration-rotation energy levels of these molecules were predicted to near the "spectroscopic" accuracy. In particular, the experimental fundamental wavenumber ν and effective rotational constant B_0 of both the isotopologues were reproduced to within about 0.5 and 0.0001 cm^{-1}, respectively.

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