



# Hyperfine constants for aluminum hydride and aluminum deuteride



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## ABSTRACT

The nuclear quadrupole coupling and spin-rotation constants of aluminum in AlH and AlD have been determined using coupled cluster theory with single and double excitations as well as perturbative inclusion of triples [CCSD(T)] combined with large correlation-consistent basis sets, cc-pCVXZ (X = T, Q and 5) and aug-cc-pCVXZ (X = T, Q). The anharmonic vibrational frequencies have been computed using second-order vibrational perturbation theory and the effects of vibrational averaging on the hyperfine constants have been determined. The ground state dipole moment has been determined for both isotopologues (AlH and AlD) and shown to depend critically on vibrational averaging. For completeness, the isotropic and anisotropic nuclear magnetic shielding tensors are also reported. All the results agree well with the best available experimental measurements, and in some cases (spin-rotation constants and dipole moments) refine the known data. The present computational results for the vibrationally averaged electric field gradients suggest that the currently accepted nuclear quadrupole moment for  $^{27}\text{Al}$  of  $146.6 \pm 1.0$  mb may be slightly underestimated. Based on the experimental measurements of the nuclear quadrupole coupling for AlH (AlD) and best computational determinations of the vibrationally averaged electric field gradients, the quadrupole moment of  $^{27}\text{Al}$  is determined to be  $149 \pm 2$  mb ( $148 \pm 3$  mb). However, this conclusion would be further strengthened with more precise experimental measurement of the  $^{27}\text{Al}$  nuclear quadrupole coupling for AlH and AlD.

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## 1. Introduction

Aluminum hydride, AlH, the “simplest” aluminum containing molecule, has intrigued spectroscopists and theoreticians for almost 100 years [1–4]. In 1956, Herbig [5] identified AlH as the emitter of bright lines (electronic transitions) observed earlier in the long-period variable star,  $\chi$  Cygni [6]. The first pure rotational spectrum of AlH was reported by Goto and Saito in 1995 [7] and provided the first estimate of the  $^{27}\text{Al}$  nuclear quadrupolar coupling constant,  $C_Q(^{27}\text{Al}) = -36.72$  MHz. In 2001, Gee and Wasylishen [8] pointed out that the analysis of this data did not include perturbations due to the  $^{27}\text{Al}$  and  $^1\text{H}$  nuclear spin-rotation interactions. Their quantum chemistry computations indicated that the  $^{27}\text{Al}$  nuclear quadrupolar coupling constant (NQCC) was significantly larger in magnitude, i.e., approximately  $-49$  MHz, and that the  $^{27}\text{Al}$  spin rotation constant,  $C_I(^{27}\text{Al})$ , was on the order of 300 kHz. Subsequent laboratory measurements by Halfen and Ziurys [9] determined that  $C_Q(^{27}\text{Al}) = -48.59(70)$  MHz and  $C_I(^{27}\text{Al}) = 306(35)$  kHz for AlH. For the isotopologue, AlD, the corresponding values were determined as  $C_Q(^{27}\text{Al}) = -48.48(88)$  MHz and  $C_I(^{27}\text{Al}) = 156(41)$  kHz. The latter values for AlD have been

revised [10] but as explained here the revised spin-rotation value is suspect.

One interesting feature concerning the electronic structure of aluminum hydride is the small HOMO–LUMO gap [11]. This property of aluminum hydride makes it challenging to compute parameters such as nuclear spin-rotation tensors and their related magnetic shielding tensors [11,12,8]. The small HOMO–LUMO gap of AlH results in a large paramagnetic contribution to the aluminum magnetic shielding perpendicular to the AlH bond (i.e., significant deshielding of the aluminum nucleus). In fact, the shielding anisotropy for AlH,  $\sigma_{\parallel} - \sigma_{\perp} \approx 1000$  ppm (vide infra) is comparable to or greater than the range of known aluminum chemical shifts [11]. Furthermore, it is interesting to mention that compared to the aluminum diatomic halides, the aluminum nucleus of AlH is significantly deshielded [12,13]; a result that may be counterintuitive if one incorrectly thinks that magnetic shielding constants are “in some way” related to electron density.

The early computations of Gee and Wasylishen [8] are not “state-of-the-art” by today’s standards and clearly need to be replaced. There have been recent ab initio multi-configuration interaction computations focussed on determining the ground state potential energy curve for AlH [14,15] and corresponding vibrational and rotational constants. However, neither of these studies have considered the hyperfine interactions critical for the understanding of the rotational spectrum of AlH (AlD). Therefore,

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the purpose of the present work is to determine, using high-level CCSD(T) computations, spectroscopic constants and the dipole moments which are related to ground electronic state ro-vibrational spectroscopy of AIH and AID. The work also presents a comprehensive collection of previous theoretical and computational results for these spectroscopic properties in order to facilitate comparison. The harmonic frequency and first-order anharmonic correction are determined to permit the computation of vibrationally-averaged properties in addition to those at the equilibrium geometry. The rotational constant and vibration–rotation coupling are computed. Importantly, both the nuclear quadrupole coupling constants (via electric field gradients) and spin-rotation constants for Al are determined using the highest-level of ab initio electronic structure theory to date. These new computational values allow the assessment of the accuracy of recent experimental measurements of the rotational spectra for AIH and AID [9,10]. Also, given that the experimental value of  $C_Q(^{27}\text{Al})$  is known more accurately [9], we are able to combine theory and experiment to propose a revised value of the nuclear quadrupole moment,  $eQ(^{27}\text{Al})$ , for the  $^{27}\text{Al}$  nucleus.

## 2. Computational methods

The calculations for AIH were carried out using coupled-cluster theory with single and double excitations as well as perturbative inclusion of triples, i.e., CCSD(T) [16–18]. Since the accurate determination of NQCCs requires a good description of the wavefunction near the nucleus, all computations have been carried out using the cc-pCVXZ and aug-cc-pCVXZ ( $X = \text{T, Q, or } 5$ ) families of basis sets [19]. Some basis sets for aluminum were obtained from the Basis Set Exchange [20,21]. In the CCSD(T) calculations, all electrons have been correlated. The EFGs determined computationally are converted to  $C_Q$  values using the nuclear quadrupole moments from Ref. [22], i.e.,  $Q(^{27}\text{Al}) = 146.6 \pm 1.0 \text{ mb}$  and  $Q(D) = 2.860 \pm 0.015 \text{ mb}$ . Our primary interest, beyond the EFGs, is in the theoretical determination of the spin-rotation constants. The spin-rotation constants have been computed previously for AIH using HF, MP2, and DFT (B3LYP) methods [8] – theoretical results have not been reported previously for AID. Therefore, we have determined the spin-rotation constants for both AIH and AID using CCSD(T) theory [23–25]. The spin-rotation constants are more difficult to determine than the EFGs because they require analytical second derivative techniques [26–29]. The isotropic/anisotropic nuclear magnetic shielding constants, which are available from the same calculations required to determine the spin-rotation constants, are also reported. All the CCSD(T) calculations have been undertaken with the CFOUR program package [30].

The vibrational averaging for molecular properties is carried out using built-in procedures in CFOUR, and its general implementation has been discussed in detail previously [31,32]. Here we present the specific application to the diatomic molecules considered here – a consideration that leads to a much simpler expression. The expectation value of the property  $X$  (i.e., the EFG, the spin-rotation constant, or the shielding tensor) is expanded over the vibrational wavefunction in a Taylor series around the equilibrium geometry with respect to bond-coordinate displacement,  $Q$  [33]:

$$\langle X \rangle = X_{eq} - \frac{1}{4\omega^{3/2}} \left( \frac{\partial X}{\partial Q} \right)_{Q=0} \phi + \frac{1}{4\omega} \left( \frac{\partial^2 X}{\partial Q^2} \right)_{Q=0} \quad (1)$$

In Eq. (1),  $\omega$  is the harmonic frequency and  $\phi$  is the corresponding cubic force constant, which is computed by numerical differentiation of analytically calculated harmonic force fields with respect to bond-coordinate displacement. The required property derivatives are also obtained via numerical differentiation of the corresponding

property values. The vibrational corrections obtained via Eq. (1) are correct to third order.

## 3. Results and discussion

In the following sections, we detail the results of the present CCSD(T) computations and compare with previous computational determinations and experimental measurements. We report properties at both the equilibrium geometries and based upon vibrational-averaging, see Eq. (1). Since vibrational averaging requires the evaluation of the harmonic frequency, equilibrium properties, and property derivatives evaluated at the equilibrium position, it is first necessary to determine the equilibrium bond length for each basis set. Table 1 reports the equilibrium bond lengths from the present work – these values will be used for all subsequent determinations of equilibrium and vibrationally-averaged properties for a given basis set. While there have been many computational determinations of the AIH equilibrium bond length [14,15,34–49], Table 1 reports selected previous high-level computational results and experimental measurements [50–54]. All the present CCSD(T) results are within 0.005 Å (0.3%) of the most recent experimental measurement [50] of 1.64735188(26) Å. Our best theoretical determination of the equilibrium bond length is within 0.07% of the experimental value. Those utilizing the largest basis set exhibit superior agreement with experiment than recent MRCI results [14,15] and are comparable to the best available ab initio value [35] and that from a composite method based upon high-level computations [34]. Therefore, the current structures provide an accurate basis for determining both equilibrium and vibrationally averaged properties.

### 3.1. Vibrational and rotational energies

In the present work, both equilibrium and vibrationally averaged properties will be determined. Hence, it is important to assess the accuracy of the vibrational averaging by determining the anharmonic vibrational energies for AIH and AID. The vibrational anharmonicity is treated using second-order perturbation

**Table 1**

Computationally determined equilibrium bond lengths as compared to previously computed and experimentally measured values.

Method	Reference	$R_e/\text{Å}$
CCSD(T)/cc-pCVTZ	This work	1.6511
CCSD(T)/cc-pCVQZ	This work	1.6458
CCSD(T)/cc-pCV5Z	This work	1.6450
CCSD(T)/aug-cc-pCVTZ	This work	1.6524
CCSD(T)/aug-cc-pCVQZ	This work	1.6465
MRCI/aug-cc-pV6Z	Ref. [14]	1.635
MRCI/cc-pV6Z	Ref. [15]	1.6707
MRCI/aug-cc-pV5Z	Ref. [15]	1.6510
W4[CCSDTQ]	Ref. [34]	1.6454
DK3-CCSDTQ/VQZ <sup>a</sup>	Ref. [35]	1.649
CCSD(T)/Al[7s7p5d4f]; H[6s4p3d]	Ref. [40]	1.6399
MRCI/cc-pV5Z	Ref. [42]	1.6508
FCI/Al[7s,5p,2d]; H[4s,3p] <sup>b</sup>	Ref. [44]	1.659
MRCI/VTZ <sup>c</sup>	Ref. [45]	1.6517
MRCI/VTZ <sup>d</sup>	Ref. [45]	1.6579
Experiment	Ref. [50]	1.64735188(26)
Experiment	Ref. [51]	1.645362224046089 (Fit)
Experiment	Ref. [52]	1.647395(51)
Experiment	Ref. [53]	1.67438(5)
Experiment	Ref. [54]	1.6482(2)

<sup>a</sup> Theoretical best estimate from DK3-CCSD, DK3-CCSDT, DK3-CCSDTQ with DZ, TZ and QZ basis sets.

<sup>b</sup> Included correlation of valence electrons only.

<sup>c</sup> With [He] core.

<sup>d</sup> With [Ne] core.

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