

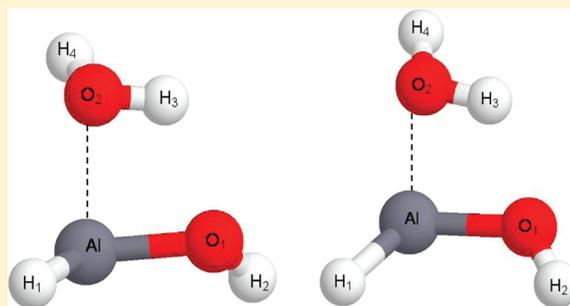
Electron Paramagnetic Resonance Spectroscopic Evidence for the Interaction of HAlOH with Water Molecules

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S Supporting Information

ABSTRACT: The complex HAlOH:(H₂O) has been detected by matrix-isolation IR spectroscopy. This complex was speculated to be the species responsible for the chemiluminescent glow associated with the explosion of trimethyl aluminum or aluminum grenades in the upper atmosphere. Theoretical studies suggest that HAlOH:(H₂O)_n is a critical precursor in the formation of H₂ in the reaction of Al with liquid water. In our study, Al atoms were reacted with mixtures of D₂O/He or H₂¹⁷O/He in an adamantane matrix in a metal-atom reactor, known as a rotating cryostat, maintained at 77 K and at <10⁻⁶ Torr. In addition to DAiOD and HAlOH, which formed from the reaction of Al atoms with adventitious water, EPR analysis of the Al–D₂O/He reaction mixture from 77 to 290 K showed that HAlOH:(D₂O) and DAiOD:(D₂O) formed. The experimental nuclear hyperfine interactions (hfis) for these species were in close agreement with those calculated using the B3LYP density functional method and the 6-311+G(2df,p) basis set. The effect of complexation is to lower the Al hfi of HAlOH and DAiOD by ca. 8%, the H hfi of HAlOH by ca. 28%, and the D hfi of DAiOD by ca. 35%.



INTRODUCTION

There has always been great interest in the reaction of metals with water because of the implication for catalytic systems. The reaction of many metals with liquid water is thermodynamically favorable.¹ For instance, the reaction of Al atoms with water results in the rapid formation of a significant amount of hydrogen. This makes the Al–water system useful in rocket propellants and in explosives. Means to increase the reactivity of Al particles with water are being investigated with the view of lowering ignition temperatures and shortening reaction times.²

Attempts have been made to better understand the nature of the intermediates, formed in the Al–water reaction, that lead to hydrogen formation. A number of experimental studies involving the Al–water reaction have appeared in the past 30 years. Oblath and Gole³ showed that the reaction of Al atoms with water vapor produced a chemiluminescent glow similar to that observed upon explosion of trimethyl aluminum or aluminum grenades in the upper atmosphere. They proposed that a complex consisting of an Al atom and several molecules of water or the Al insertion product, HAlOH, was responsible for the chemiluminescent glow.

Margrave and co-workers used IR⁴ and UV–vis⁵ spectroscopy to study the products formed upon co-condensing Al atoms with water in a Kr matrix at 15 K. The major product formed at low water concentration, HAlOH, resulted from the spontaneous insertion of the Al atom in the H–O bond of water. The absorption band observed in the UV–vis spectrum of HAlOH⁵ correlated well with the chemiluminescent emission reported by Oblath and Gole.³ At higher water

concentration, Margrave and co-workers⁴ detected an additional three IR bands that were tentatively assigned to the Al–O and Al–OH stretching vibration and to the HAlO bending vibration of HAlOH:(H₂O).

Evidence for the formation of HAlOH was also obtained by matrix-isolation EPR spectroscopy.^{6,7} The co-condensation of Al atoms with the isotopomers of water, that is, D₂O and H₂¹⁷O, in Ne, Ar,⁶ or adamantane,⁷ produced spectral changes consistent with the formation of DAiOD and HAl¹⁷OH, respectively, and confirmed the formation of HAlOH.

A number of theoretical studies concerning the reaction of Al with water have also appeared.^{8–11} In all of the studies involving the reaction of neutral Al atoms with water, the most stable product was shown to be HAlOH.⁸ However, the formation of HAlOH from the collision of Al with water was put in question because the energy barrier was too high for this to be the favored reaction route. The fact that HAlOH spontaneously formed in the IR and EPR matrix-isolation experiments was thought to occur because (a) Al and water are trapped, which forces AlOH₂ to be a long-lived adduct, or (b) the matrix may provide the energy necessary to overcome the transition state barrier.

In a subsequent investigation,⁹ the potential energy surface of Al(H₂O)_{n+1} (*n* = 0–3) was shown to have low lying local minima when Al interacts with more than one water molecule.

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Isomerization of $\text{AlOH}_2:(\text{H}_2\text{O})_n$ results in the formation of the complexed insertion product $\text{HALOH}:(\text{H}_2\text{O})_{n-1}$. The association of Al atoms with more than one water molecule appears to have a catalytic effect. It is therefore puzzling that we have not been able to detect these type of complexes in the Al atom–water reactions carried out in our laboratory. The authors⁹ have suggested that $\text{HALOH}:(\text{H}_2\text{O})_{n-1}$ can proceed to form either $\text{Al}(\text{OH})_2:(\text{H}_2\text{O})_{n-2} + \text{H}_2$ or $\text{AlOH}:(\text{H}_2\text{O})_{n-1} + \text{H}$. The second pathway generates H_2 and hydrated $\text{Al}(\text{OH})_2$ via the recombination of two H atoms, for systems where $n > 2$.

Complexed divalent Al compounds have been observed by EPR spectroscopy under matrix isolation conditions. These include $\text{HAlNH}_2:(\text{NH}_3)$ ¹² and $\text{CpNH}(\text{AlH}):(\text{CpNH}_2)$ ¹³ formed in the Al atom reactions of NH_3 and cyclopropylamine (CpNH_2), respectively. Knowing that Al in divalent compounds can form complexes with molecules containing a lone pair of electrons, HALOH could possibly interact with H_2O under our experimental conditions. To test this hypothesis, Al atoms were reacted with a mixture of $\text{D}_2\text{O}/\text{He}$ or $\text{H}_2^{17}\text{O}/\text{He}$ at 77 K in an adamantane matrix. EPR spectra were recorded at 10 K intervals as the reaction mixtures were annealed from 77 to 290 K in the cavity of the EPR spectrometer. We report herein the first EPR evidence for the formation of $\text{HALOH}:(\text{H}_2\text{O})$, an intermediate that is thought to be critical in the formation of H_2 in the Al–water reaction. Density functional theory calculations of the nuclear hyperfine interaction (hfi) of $\text{HALOH}:(\text{H}_2\text{O})$ were used to support our spectral assignment. More specifically, a_{Al} and a_{H} values, determined for the cis and trans conformers of HALOH and $\text{HALOH}:(\text{H}_2\text{O})$ using the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d,p) method, were compared to the experimental nuclear hfi values.

EXPERIMENTAL SECTION

Materials. In this study, Al atoms, generated by the resistive heating of Al wire (Fisher, >99.9%), were co-condensed with adamantane (Aldrich, >99%) and D_2O (Cambridge Isotopes Laboratories, D \approx 99.9%) or H_2^{17}O (Cambridge Isotopes Laboratories, $^{17}\text{O} \approx 70\%$) diluted in He. The substrates and adamantane were degassed using several freeze–thaw cycles with the aid of a vacuum line. $\text{D}_2\text{O}/\text{He}$ (1:39) and $\text{H}_2^{17}\text{O}/\text{He}$ (1:37) mixtures were prepared using a vacuum line.

Preparation of the Al Atom Reaction Mixtures. The reaction mixtures were prepared with the aid of a metal atom reactor known as a rotating cryostat. The design and operation of the rotating cryostat has been described in detail previously by Bennett et al.¹⁴ During an experiment, the liquid N_2 -filled drum, suspended inside the reaction chamber, was rotated at ca. 2000 rpm. The pressure inside the chamber was maintained at $<1.33 \times 10^{-6}$ mbar. The $\text{D}_2\text{O}/\text{He}$ (1:39) or $\text{H}_2^{17}\text{O}/\text{He}$ (1:37) mixture and adamantane, introduced into the reaction chamber via portholes, were condensed onto the surface of the cold drum (77 K). Al atoms were produced from ca. 30 mg of Al wire placed in a tungsten basket (no. 12070, Ernest F. Fullam, Schenectady, NY) suspended between the two electrodes of a furnace previously described by Buck et al.¹⁵ Typically, 10^{-1} mbar of the reactants, introduced via a needle valve assembly, and 1.33 mbar of the adamantane were introduced into the reaction chamber of the cryostat. A typical experiment lasted for approximately 10 min. A sample of each reaction mixture was scraped off the drum into a quartz Suprasil EPR tube, under vacuum, at 77 K. The tube was sealed and stored in a liquid N_2 storage Dewar pending EPR analysis.

EPR Analysis. EPR spectra were recorded at 77 K on a Varian E109 EPR spectrometer operating at X-band. In experiments in which the spectra were recorded as a function of temperature, the cavity, fitted with a quartz insert, was refrigerated with the aid of a liquid N_2 evaporator. The quartz insert was equipped with a heater and a silicon diode temperature sensor. A Lakeshore 330 Series autotuning temperature controller was used to heat the cold N_2 gas passing through the cavity to the desired temperature.

The spectra were collected using the digital output of the spectrometer with the aid of EPRWare (Scientific Software Services, Bloomington, IL). Spectra were calibrated with a Varian gaussmeter, and the frequencies corresponding to the field measurements were determined with a Systron-Donner 6016 frequency counter.

Determination of the Magnetic Parameters. The nuclear hfi, g -value, and the corresponding standard deviations, for the species observed in the Al atom reactions, were determined by solving the isotropic spin Hamiltonian with the aid of the ESRLSQ software.¹⁶ More specifically, the magnetic field position of the transition lines of each species obtained from calibrated spectra as well as the frequencies at which they were recorded were entered into the ESRLSQ program. The program provides the nuclear hfi and the g -values of the species by solving the Breit–Rabi equation.¹⁷

Density Functional Theory (DFT) Calculations. The nuclear hfi's of a number of Al atom–water insertion products were calculated using a density functional theory (DFT) method. The B3LYP¹⁸ functional, which combines Becke's three-parameter exchange functional¹⁹ with Lee, Yang, and Parr's correlation functional,²⁰ and the split valence 6-31G(d,p) basis set were used to optimize the geometry of several isomers of possible products. All of the isomers were characterized as minimum energy conformers using frequency analysis to distinguish them from transition-state geometries. The energies and nuclear hfi of the isomers were calculated using the B3LYP functional with the 6-311+G(2df,p) basis set. The above-mentioned functional and basis sets were available in the Gaussian 98W software package.²¹

The zero-point potential energy (E_1) of the conformers was calculated from the potential energy of the conformers optimized with the B3LYP functional and the 6-311+G(2df,p) basis set in kcal/mol (E_0) using eq 1:

$$E_1 = \left[E_0 + \sum_{n=1}^{n_{\text{tot}}} \frac{hc\nu_n}{2} \right] \frac{N_A}{4184} \quad (1)$$

where h is Planck's constant, n_{tot} is the number of calculated vibrational normal modes, ν_n is a normal frequency (cm^{-1}), calculated using the B3LYP functional with the 6-31G(d,p) basis set, N_A is Avogadro's number, and c is the speed of light (3×10^{10} cm/s).

RESULTS

Al/Deuterium Oxide (D_2O)/He/Adamantane. The EPR spectrum of the paramagnetic products of the reaction of Al atoms with $\text{D}_2\text{O}/\text{He}$ (1:39), recorded at 77 K, was dominated by a 16-lined pattern with a spacing of 41 G (115 MHz) centered at $g = 2.0023$ characteristic of the well-known Al trimer, Al_3 .²² At this temperature, at least three mononuclear aluminum species were detected. Upon warming the sample to 100 K, the signals for these three species resolved, due to the onset of rotational motion in the adamantane matrix, Figure 1,

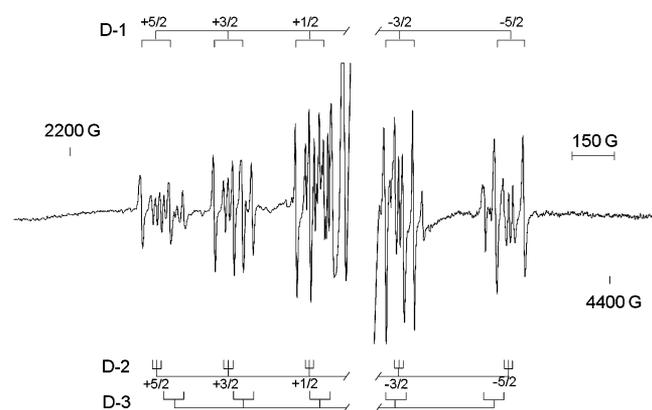


Figure 1. EPR spectrum recorded at 100 K of the sample collected from the reaction of Al atoms with the D₂O/He (1:39) mixture in an adamantane matrix ($\nu = 9.1372$ GHz; microwave power (m.p.) = 2 mW).

to give a sextet of doublets (D-1) centered at $g = 2.0014 \pm 0.0001$ with $a_{\text{Al}} = 914.0 \pm 0.2$ MHz and $a_{\text{H}} = 281.6 \pm 0.1$ MHz, a sextet of triplets (D-2) centered at $g = 2.0011 \pm 0.0002$ with $a_{\text{Al}} = 911.8 \pm 0.5$ MHz and $a_{\text{D}} = 40.3 \pm 0.1$ MHz, as well as a sextet of doublets (D-3) with $g = 2.0017 \pm 0.0001$, $a_{\text{Al}} = 843.6 \pm 0.1$ MHz, and $a_{\text{H}} = 188.7 \pm 0.3$ MHz. The ratio of the a_{H} (D-1) to a_{D} (D-2) is $281.6/40.3$ or 6.98 (close to the ratio of the gyromagnetic ratios of H and D).

Further resolution of the spectrum was observed at 140 K, where an additional four species appeared; these are labeled D-4–D-7 in Figure 2. D-4 presents as a sextet of triplets (as was

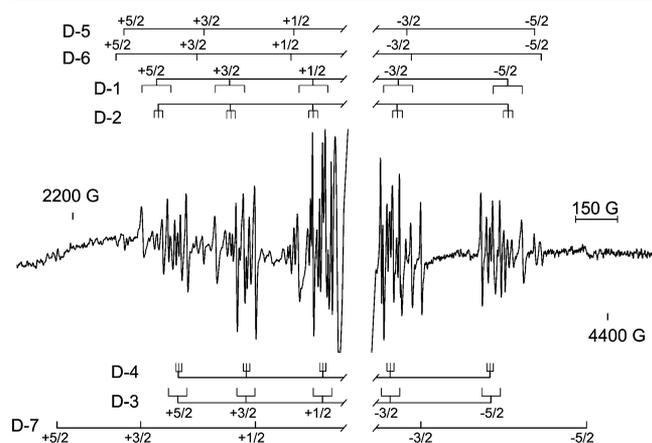


Figure 2. EPR spectrum recorded at 140 K of the sample collected from the reaction of Al atoms with a D₂O/He (1:39) mixture in an adamantane matrix ($\nu = 9.1232$ GHz; m.p. = 2 mW).

observed for D-2) centered at $g = 2.0018 \pm 0.0001$ with $a_{\text{Al}} = 841.4 \pm 0.2$ MHz and $a_{\text{D}} = 28.9 \pm 0.4$ MHz. The sextets labeled D-5, D-6, and D-7 do not possess any super hyperfine interaction (super hfi); their g and a_{Al} values were found to be 2.0020 ± 0.0002 and $a_{\text{Al}} = 1038.1 \pm 0.4$ MHz for D-5, 1.9995 ± 0.0024 and $a_{\text{Al}} = 1061.7 \pm 5.8$ MHz for D-6, and 2.0023 ± 0.0008 and $a_{\text{Al}} = 1274.5 \pm 2.0$ MHz for D-7. The transitions belonging to each of these species can be seen in Figure 2.

The $M_I = 1/2$ transition lines of species D-1–D-4, recorded at 140 K, Figure 3, better illustrate the super hfi. This figure also shows the high degree of overlap of the signals belonging to species D-1, D-2, D-3, and D-4. At 160 K, species D-1 and D-2

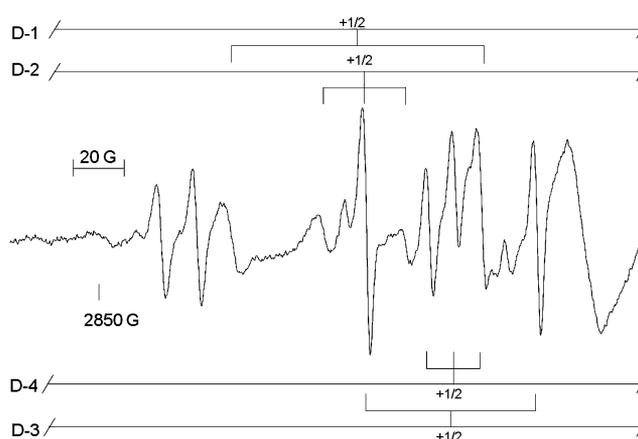


Figure 3. The EPR spectrum recorded at 140 K of the Al $M_I = 1/2$ transition lines for species D-1, D-2, D-3, and D-4 identified in the reaction of Al atoms with a D₂O/He (1:39) mixture in an adamantane matrix ($\nu = 9.1233$ GHz; m.p. = 2 mW).

have decomposed and are no longer visible, while species D-3 and D-4 disappear at 220 K. A summary of the magnetic parameters of the species detected in the Al atom D₂O reaction is found in Table 1.

Table 1. Magnetic Parameters Extracted from the EPR Spectra of the Species Produced in the Reaction of Al Atoms with a D₂O/He (1:39) Mixture in an Adamantane Matrix

species	g value	a_{Al} (MHz)	super hfi (MHz)	assignment
D-1	2.0014	914.0	281.6 (1H)	HAIOH
D-2	2.0011	911.8	40.3 (1D)	DAIOD
D-3	2.0017	843.6	188.7 (1H)	HAIOH:(D ₂ O)
D-4	2.0018	841.4	28.9 (1D)	DAIOD:(D ₂ O)
D-5	2.0020	1038.1		
D-6	1.9995	1061.7		
D-7	2.0023	1274.5		

Al/¹⁷O–Water (H₂¹⁷O)/Adamantane. The Al atom reaction was repeated with a mixture of H₂¹⁷O/He (1:37) under the same conditions outlined above. At 77 K, the spectrum was dominated by Al₃; a mononuclear Al species, ¹⁷O-1, was also detected. Upon warming the sample to 120 K, the transition lines of this species resolved, Figure 4, giving a sextet of doublets centered at a g -value of 2.0010 ± 0.0001 with an a_{Al} of 917.2 ± 0.2 MHz and a a_{H} of 287.5 ± 0.8 MHz. Two additional species were detected at 120 K, that is, ¹⁷O-2 and ¹⁷O-3, Figure 4. The sextet of doublets centered at $g = 2.0019 \pm 0.0001$ with $a_{\text{Al}} = 862.8 \pm 0.1$ MHz and $a_{\text{H}} = 179.4 \pm 0.4$ MHz has been attributed to species ¹⁷O-2, while the sextet of doublets centered at $g = 2.0020 \pm 0.0003$ with $a_{\text{Al}} = 843.8 \pm 0.6$ MHz and $a_{\text{H}} = 187.6 \pm 2.2$ MHz has been assigned to species ¹⁷O-3.

At 130 K, the EPR transition lines of species ¹⁷O-2 were no longer visible. At 160 K, four new weak sextets were detected, labeled ¹⁷O-4–¹⁷O-7. The magnetic parameters were estimated to be: $g = 1.9997 \pm 0.0009$ and $a_{\text{Al}} = 1037.2 \pm 2.2$ MHz (¹⁷O-4); $g = 1.9946 \pm 0.0019$ and $a_{\text{Al}} = 1068.6 \pm 4.6$ MHz (¹⁷O-5); $g = 2.0013 \pm 0.0007$ and $a_{\text{Al}} = 1270.1 \pm 2.2$ MHz (¹⁷O-6); and $g = 2.0023 \pm 0.0005$ and $a_{\text{Al}} = 1283.6 \pm 1.4$ MHz (¹⁷O-7). Additional super hfi was not observed for these four species. It is important to note that species ¹⁷O-3 was no longer visible at 160 K. Further annealing of the sample resulted in the

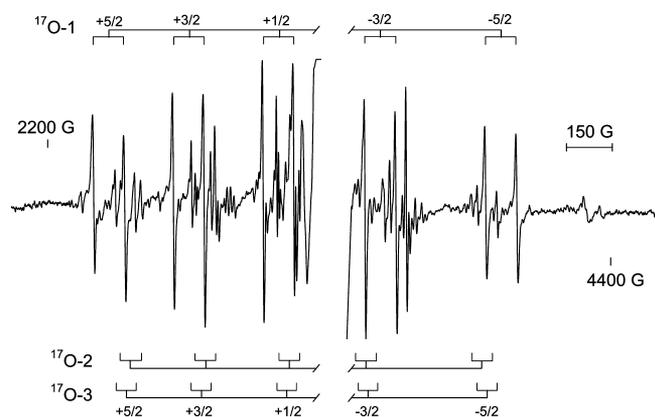


Figure 4. EPR spectrum recorded at 120 K of the sample collected from the reaction of Al atoms with a $\text{H}_2^{17}\text{O}/\text{He}$ (1:37) mixture in an adamantane matrix ($\nu = 9.1204$ GHz; m.p. = 2 mW; ratio of the receiver gain at high field to low field (L/H) = 1.3; center omitted).

disappearance of the spectra for ^{17}O -1 at 180 K, ^{17}O -7 at 190 K, ^{17}O -4 and ^{17}O -5 at 200 K, and ^{17}O -6 at 260 K. A summary of the magnetic parameters of the species detected in the Al atom- H_2^{17}O reaction is found in Table 2.

Table 2. Magnetic Parameters Extracted from the EPR Spectra of the Species Produced in the Reaction of Al Atoms with a $\text{H}_2^{17}\text{O}/\text{He}$ (1:37) Mixture in an Adamantane Matrix

species	g value	a_{Al} (MHz)	super hfi (MHz)	assignment
^{17}O -1	2.0010	917.2	287.5 (1H)	HAIOH
^{17}O -2	2.0019	862.8	179.4 (1H)	HAIOH:(H_2O) ^a
^{17}O -3	2.0020	843.8	187.6 (1H)	HAIOH:(H_2O)
^{17}O -4	1.9997	1037.2		
^{17}O -5	1.9946	1068.6		
^{17}O -6	2.0013	1270.1		
^{17}O -7	2.0023	1283.6		

^aIt is speculated that ^{17}O -2 and ^{17}O -3 are the same species trapped in different sites of the adamantane matrix.

Density Functional Theory (DFT) Calculations of HAIOH and HAIOH:(H_2O). The nuclear hfi's of HAIOH and HAIOH:(H_2O) were calculated using a density functional theory (DFT) method. In general, the geometries of several isomers of HAIOH and HAIOH:(H_2O) were optimized using the B3LYP functional and the split valence 6-31G (d,p) basis set. All of these species were characterized as minimum energy conformers using frequency analysis. The energies and nuclear hfi of the isomers were calculated using the B3LYP functional with the 6-311+G (2df,p) basis set.

i. HAIOH. The structural data for the optimized geometries of *cis* and *trans* HAIOH (Chart 1) are presented in Table S1 (Supporting Information). The initial geometries were based on previous theoretical work⁶ on the HAIOH molecule using Gaussian 90 with the MP2/6-31G method.

Despite the fact that the bond lengths and bond angles of the *cis* and *trans* isomers are very similar, there are large differences in the calculated hfi values, Table 3; the a_{Al} , a_{H1} , and a_{H2} of the *trans* isomer are 176.1, 6.3, and 25.9 MHz smaller than that of the *cis* isomer, respectively. A comparison of the zero-point energy of these two molecules indicates that the *trans* isomer is about 1 kcal/mol lower in energy than the *cis* isomer.

Chart 1

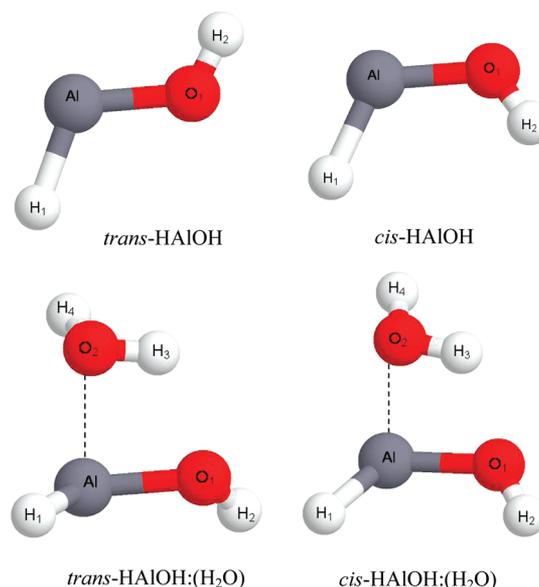


Table 3. Nuclear hfi and Potential Energies Calculated for the *Trans* and *Cis* Isomers of HAIOH Using the B3LYP Functional and the 6-311+G (2df,p) Basis Set

	nuclear hfi (MHz)	
	<i>trans</i> HAIOH	<i>cis</i> HAIOH
H_1	284.6	290.9
Al	865.3	1041.4
O	-11.7	-74.2
H_2	-3.8	29.7
zero-point energy (kcal/mol)	-200 112.3	-200 111.3

ii. HAIOH:(H_2O) Complex. A study was undertaken to look at the geometry, the nuclear hfi, and the energies of possible HAIOH:(H_2O) complexes. Despite using several different conformations as a starting point for the calculations, only two were considered plausible according to the frequency analysis (Chart 1). The structural data obtained for these isomers, the *trans* and *cis* isomers, optimized using the B3LYP functional and the 6-31G(d,p) basis set are presented in Table S2 (Supporting Information).

The a_{Al} of the *cis* complex is 118.5 MHz larger than that of the *trans* complex. The a_{H} of the hydrogen atom directly bonded to the Al atom is large for both isomers. However, a_{H1} for the *cis* complex is 2 MHz larger than that of the *trans* complex. From the zero-point energy, the *cis* and *trans* isomers differ by less than 1 kcal/mol, Table 4.

DISCUSSION

Al Insertion Product of Water. Al atoms have been shown to react with water to form HAIOH.⁴ In fact, there are numerous examples where HAIOH forms from the reaction of Al atoms with the residual water present in the metal atom reactor.^{7,23,24} Interestingly, increasing the amount of water during an experiment does not increase the amount of HAIOH found.⁷ This is presumably due to the fact that the concentration of monomeric H_2O remains low due to hydrogen bonding.⁷ Past work has shown that the HAIOH radical gives a characteristic EPR spectrum consisting of a sextet of doublets centered at $g = 1.9998 \pm 0.0004$ with $a_{\text{Al}} = 911 \pm 6$

Table 4. Nuclear hfi and Potential Energies Calculated for the Trans and Cis Isomers of the HAlOH:(H₂O) Complex Using the B3LYP Functional and the 6-311+G (2df,p) Basis Set

	nuclear hfi (MHz)	
	trans	cis
Al	786.2	904.7
H ₁	206.9	208.9
H ₂	-2.3	7.9
H ₃	-0.3	0.5
H ₄	-2.1	-3.1
O ₁	-14.7	-45.7
O ₂	-22.8	-41.7
zero-point energy (kcal/mol)	-248 088.3	-248 088.6

MHz and $a_{\text{H}} = 286 \pm 4$ MHz.⁷ The species labeled D-1 (D₂O/He experiment), and ¹⁷O-1 (H₂¹⁷O/He experiment), Tables 1 and 2, obtained in this study, have magnetic parameters that match very closely with those reported for HAlOH. The trace of H₂O in the cryostat as well as that found in the reactants, that is, D₂O and H₂¹⁷O (¹⁷O enrichment is only 70%), is responsible for the HAlOH observed.

Knight et al. confirmed the formation of HAlOH by repeating the Al atom reactions with D₂O ($I_{\text{D}} = 1$)⁶ and H₂¹⁷O ($I_{17\text{O}} = 5/2$),⁶ respectively. The isotopic analogues of HAlOH were identified as DAiOD, a sextet of triplets, with $a_{\text{Al}} = 917$ MHz and $a_{\text{D}} = 44$ MHz, and HAl¹⁷OH, a sextet of doublets of sextets, with $a_{\text{Al}} = 917$ MHz, $a_{\text{H}} = 288$ MHz, and $a_{17\text{O}} = 13$ MHz.⁶ The change in hfi in going from H to D was consistent with the change in gyromagnetic ratios of H and D.¹⁷

In our study, species D-2, produced in the Al atom–D₂O experiment, was identified as a sextet of triplets with $a_{\text{Al}} = 911.8$ MHz and $a_{\text{D}} = 40.3$ MHz, belonging to DAiOD. It was anticipated that a species with magnetic parameters similar to those of HAl¹⁷OH would also be produced in the Al atom–H₂¹⁷O experiment. Unfortunately, this was not the case. This could be due to the fact that the ¹⁷O hfi produces very weak transition lines, making them difficult to distinguish from the baseline, and to the large degree of signal overlap prevalent in the spectra at this temperature.

The calculated Al and H hfi of the trans and cis isomers of HAlOH can be compared to values obtained in previous theoretical studies^{6,7,25–27} (Table 5). As expected, the studies that conducted calculations at identical levels of theory produced very similar values. The closest agreement between the experimental a_{Al} value for HAlOH, that is, $a_{\text{Al}} = 915$ MHz and $a_{\text{H}} = 286$ MHz, and theory was obtained with the PWP86/IGLO-III//QCISD/6-31G(d,p) method; the calculated a_{Al} and a_{H} for the trans isomer differed from the experimental values by 4% and 2%, respectively.²⁷ The B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d,p) method also gave very good approximations, with a_{Al} (trans) and a_{H} (trans) differing from the experimental values by about 5% and 1%, respectively. A comparison of the theoretical calculations presented in Table 5 shows that $a_{\text{Al}}(\text{cis}) > a_{\text{Al}}(\text{trans})$; $a_{\text{Al}}(\text{trans})$ varies from 811 to 881 MHz, while $a_{\text{Al}}(\text{cis})$ varies from 992 to 1062 MHz.

Summarizing, the best agreement between the experimental a_{Al} and a_{H} values of HAlOH and those predicted by theory was found for the trans isomer. The experimental a_{Al} value is underestimated by DFT methods, and the a_{Al} values calculated for the cis isomer are larger than that of the trans isomer.

Table 5. Comparison of the Calculated Magnetic Parameters for HAlOH

isomer	a_{Al} (MHz)	a_{H} (MHz)	level of theory	reference
trans	865	285	B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d,p)	current study
cis	1041	291		
trans	843	231	UMP2/6-311G**//UHF/6-31G*	Cramer ²⁵
trans	871	188	MP2/6-31G (d,p)	Knight, Jr. et al. ⁶
cis	1062	189		
trans	847	185	UHF/6-311G** and CISD double- ζ	Joly et al. ⁷
cis	1030	186		
trans	865	284	B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d,p)	Joly et al. ²⁶
cis	1041	291		
trans	811	249	BWP91/6-311+G(2df,p)//B3LYP/6-31G(d,p)	
cis	992	255		
trans	839	250	MPW1PW91/6-311+G(2df,p)//B3LYP/6-31G(d,p)	
cis	1006	254		
trans	816	254	BP86/6-311+G(2df,p)//B3LYP/6-31G(d,p)	
cis	997	261		
trans	881	228	MP2/6-311+G(2df,p)//MP2/6-31G(d,p)	Fängström et al. ²⁷
cis	1034	231		
trans	865	244	QCISD/6-311+G(2df,p)//MP2/6-31G(d,p)	
cis	1015	248		
trans	863	286	B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d,p)	
cis	1040	293		
trans	878	291	PWP86/IGLO-III//QCISD/6-31G(d,p)	
cis	1049	304		

HAlOH:H₂O Complexes. A matrix isolation infrared spectroscopic study⁴ involving the reaction of Al atoms with water showed that HAlOH forms complexes with water, HAlOH:(H₂O). The shift of the Al–OH bending vibration of HAlOH to a lower wavenumber as well as the detection of an Al–O stretching vibration suggested that the Al of HAlOH was coordinated to the O atom of a water molecule.⁴ This complexation reaction was supported by a DFT study in which the stability of the transition states and product states was examined for this reaction.²⁸

In the present work, these structures have been reoptimized by the B3LYP/6-311+G(2df,p)//B3LYP/6-31G(d,p) method and their nuclear hfi values compared to the values obtained from the DFT calculations of HAlOH (Table 3 vs Table 4). In general, complexation of a water molecule causes a_{Al} and a_{H} to decrease. The a_{Al} and a_{H} of *trans* HAlOH decrease from 865 and 285 MHz to 786 MHz (9%) and 207 MHz (27%), respectively. In the case of *cis* HAlOH, where $a_{\text{Al}} = 1041$ MHz and $a_{\text{H}} = 291$ MHz, complexation causes the a_{Al} and a_{H} to decrease to 905 MHz (13%) and 209 MHz (28%), respectively.

The decrease in the magnitude of the nuclear hfi upon complexation was observed for the products of the Al atom–NH₃ reaction.¹² The study showed that the a_{Al} (949 MHz) and the a_{H} (51 MHz) of the divalent aluminum radical, HAlNH₂, was reduced to 778 MHz (18%) and 37 MHz (27%), respectively, when complexed by an NH₃ molecule, forming the HAlNH₂:(NH₃) complex. This observation was echoed in the Al atom reaction of CpNH₂.¹³ The a_{Al} (962 MHz) and a_{H} (216 MHz) of the divalent N–H insertion product, CpNH–(AlH), were reduced to 801 MHz (17%) and 133 MHz (38%), respectively, by complexation of a CpNH₂ molecule, forming the CpNH(AlH):(CpNH₂) complex.¹³ This observation was

further supported by DFT calculations of the a_{Al} for $\text{CpNH}(\text{AlH})$ and $\text{CpNH}(\text{AlH}):(\text{CpNH}_2)$. The calculations predicted that complexation of a CpNH_2 molecule to $\text{CpNH}(\text{AlH})$ decreases the a_{Al} and a_{H} by 11% and 47%, respectively.¹³

Because the EPR spectrum of D-3, ^{17}O -2, and ^{17}O -3 resembles that of HALOH and their a_{Al} and a_{H} are significantly smaller than those of HALOH , we propose that D-3, ^{17}O -2, and ^{17}O -3 are complexes of HALOH , that is, $\text{HALOH}:(\text{X})$, where X is H_2O or D_2O . The fact that two such species, ^{17}O -2 and ^{17}O -3, were found in the H_2^{17}O experiment suggests that either (a) two conformations of the $\text{HALOH}:(\text{H}_2\text{O})$ complex differing slightly in the values of their nuclear hfi are formed or (b) the $\text{HALOH}:(\text{H}_2\text{O})$ complex is trapped in two different substitutional sites of the adamantane matrix,⁵ accounting for the 2–3% difference observed in the nuclear hfi. Support for the latter comes from the fact that the deviation in the magnetic parameters is slight, 2–3%, while the DFT calculations predict much greater changes (13%) in the a_{Al} in going from the cis to the trans conformation. In addition, it is important to note that species ^{17}O -2 was short-lived and disappeared by 130 K.

The experimental a_{Al} and a_{H} of HALOH differ by about 8% and 34–35%, respectively, from those of D-3 and ^{17}O -3. The DFT calculations predict that HALOH complexation results in a 9–13% decrease in the a_{Al} and a 27–28% decrease in the a_{H} . The close agreement between the calculated and experimental nuclear hfi of HALOH and $\text{HALOH}:(\text{H}_2\text{O})$ is consistent with our spectral assignments.

Additional support for this assignment arises from the species labeled D-4 in the $\text{D}_2\text{O}/\text{He}$ experiment, Figure 2. A sextet of triplets with a g value and a_{Al} very similar to those of the $\text{HALOH}:(\text{H}_2\text{O})$ complex was observed. The triplet splitting of 28.9 MHz, due to the interaction of the unpaired electron, is 6.6 times smaller than the hydrogen hfi of $\text{HALOH}:(\text{H}_2\text{O})$. D-4 is therefore assigned to $\text{DALOD}:(\text{D}_2\text{O})$ or $\text{DALOD}:(\text{H}_2\text{O})$.

Species with nuclear hfi values similar to those of $\text{HALOH}:(\text{H}_2\text{O})$ were observed in the Al atom reactions of diethyl ether (DEE) and methylethyl ether (MEE).²⁹ In experiments where mixtures of $\text{MEE}/\text{H}_2^{17}\text{O}/\text{He}$ and $\text{DEE}/\text{H}_2^{17}\text{O}/\text{He}$ were reacted with Al atoms, we detected a sextet of doublets of sextets consistent with the interaction of the unpaired electron on Al ($I = 5/2$), with one H ($I = 1/2$) nucleus and one ^{17}O ($I = 5/2$) nucleus, not unlike what was observed for HAL^{17}OH . However, the a_{Al} and a_{H} were about 10% and 46% smaller than that of HALOH , which led us to the conclusion that $\text{HAL}^{17}\text{OH}:(\text{MEE})$ and $\text{HAL}^{17}\text{OH}:(\text{DEE})$ form in line with what we observed here for $\text{HALOH}:(\text{H}_2\text{O})$.

The spin density (ρ_s) on the Al and H of HALOH and $\text{HALOH}:(\text{H}_2\text{O})$ can be estimated by dividing the experimental a_{Al} and a_{H} by those calculated for an electron in the 3s orbital of Al (3911 MHz) and the 1s orbital of H (1420 MHz).¹⁷ For HALOH , ρ_{3s} and ρ_{1s} are 0.23 and 0.20, respectively, while values of 0.22 (ρ_{3s}) and 0.13 (ρ_{1s}) were estimated for $\text{HALOH}:(\text{H}_2\text{O})$. Because complexation has the effect of reducing the delocalization of the spin density onto H and only a slight change in ρ_{3s} is observed, this presumably means that the semioccupied molecular orbital of $\text{HALOH}:(\text{H}_2\text{O})$ has increased p character. The donation of electron density from the oxygen of the water molecule to the 3 p orbitals of Al accounts for the observed decrease in the a_{Al} .

There still remains a number of species that could not be identified in the Al atom reactions carried out in this study. It is known that these are mononuclear aluminum species because

they all present a large sextet, which in these experiments could only be attributed to the interaction of an unpaired electron with the Al nucleus. The absence of additional super hfi makes it impossible to identify these species with any certainty. The fact that the a_{Al} of the remaining species is greater than that of HALOH suggests that the ligands are more electronegative or electron withdrawing than H and OH.³⁰ Knight et al. have determined that $\text{Al}(\text{OH})_2$, formed upon photo irradiation of Ne matrices containing Al atoms and H_2O , has an a_{Al} value of 1220 MHz.³⁰ The species in the above-mentioned experiments, with an a_{Al} value nearest to that of $\text{Al}(\text{OH})_2$, are D-7, D-8, ^{17}O -6, and ^{17}O -7. They differ from the $\text{Al}(\text{OH})_2$ value by 4–5%, respectively. Because the parameters in this study were determined from spectra recorded at 140–160 K, it is possible that this small deviation may be due to a temperature effect, because Knight et al. carried out their experiments at 4 K. However, it is not possible to confirm the assignment without further information.

CONCLUSION

In this study, ground-state Al atoms were reacted with D_2O and H_2^{17}O . EPR analysis of the reaction mixtures indicated that:

- (1) HALOH is formed in all of the metal atom reactions carried out in this study. DALOD was also formed in the D_2O experiment.
- (2) The lone pair electrons on the O of H_2O or D_2O are used to complex with the Al atom of HALOH resulting in $\text{HALOH}:(\text{X})$, where X = H_2O or D_2O . In the D_2O experiment, there is evidence for the formation of $\text{DALOD}:(\text{D}_2\text{O})$. This is the first EPR evidence for the formation of these types of HALOH complexes.
- (3) Complexation of the Al atom of HALOH by H_2O or D_2O causes the Al and H hfi to decrease by 8% and 34–35%, respectively.

The nuclear hfi of the Al-centered radicals produced in this study was estimated using a DFT method. More than one conformation was obtained for each of the radicals; however, the best agreement with experiment was obtained for the trans conformation. DFT calculations also predicted that the complexation of molecules containing lone pair donor atoms to the Al atom of HALOH causes a significant decrease in the Al and H hfi.

ASSOCIATED CONTENT

Supporting Information

Tables S1 and S2 contain the optimized geometries of the HALOH and $\text{HALOH}:(\text{H}_2\text{O})$ isomers used in the calculation of the nuclear hfi and potential energies. Full author list for ref 21. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Risha, G. A.; Sabourin, J. L.; Yang, V.; Yetter, R. A.; Son, S. F.; Tappan, B. C. *Combust. Sci. Technol.* **2008**, *180*, 2127–2142.
- (2) Ramaswamy, A. L.; Kaste, P. J. *Energ. Mater.* **2005**, *23*, 1–25.
- (3) Oblath, S. B.; Gole, J. L. *J. Chem. Phys.* **1979**, *70*, 581–582.
- (4) Hauge, R. H.; Kauffman, J. W.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6005–6011.
- (5) Douglas, M. A.; Hauge, R. H.; Margrave, J. L. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1533–1553.
- (6) Knight, L. B., Jr.; Gregory, B.; Cleveland, J.; Arrington, C. A. *Chem. Phys. Lett.* **1993**, *204*, 168–174.
- (7) Joly, H. A.; Howard, J. A.; Tomietto, M.; Tse, J. S. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3145–3151.
- (8) Álvarez-Barcia, S.; Flores, J. R. *J. Chem. Phys.* **2009**, *131*, 174307[1–11].
- (9) Álvarez-Barcia, S.; Flores, J. R. *Chem. Phys.* **2010**, *374*, 131–137.
- (10) Álvarez-Barcia, S.; Flores, J. R. *Chem. Phys.* **2011**, *382*, 92–97.
- (11) Álvarez-Barcia, S.; Flores, J. R. *J. Chem. Phys.* **2011**, *134*, 244305[1–7].
- (12) Kasai, P. H.; Himmel, H.-J. *J. Phys. Chem. A* **2002**, *106*, 6765–6774.
- (13) Joly, H. A.; Ashley, J.; Levesque, M. Y.; Rank, J. P. *J. Phys. Chem. A* **2006**, *110*, 3911–3919.
- (14) Bennett, J. E.; Mile, B.; Thomas, A.; Ward, B. *Adv. Phys. Org. Chem.* **1970**, *8*, 1–77.
- (15) Buck, A. J.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 3381–3387.
- (16) Preston, K.; Morton, J. R. *ESR/SQ*; National Research Council: Ottawa, ON, 1989.
- (17) Weltner, W., Jr. *Magnetic Atoms and Molecules*; Dover: New York, 1989.
- (18) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648[1–5].
- (20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; et al. *Gaussian 98W*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (22) Howard, J. A.; Sutcliffe, R.; Tse, J. S.; Dahmane, H.; Mile, B. *J. Phys. Chem.* **1985**, *89*, 3595–3598.
- (23) Howard, J. A.; Joly, H. A.; Edwards, P. P.; Singer, R. J.; Logan, D. E. *J. Am. Chem. Soc.* **1992**, *114*, 474–477.
- (24) Mile, B.; Howard, J. A.; Tse, J. S. *Organometallics* **1988**, *7*, 1278–1282.
- (25) Cramer, C. J. *J. Mol. Struct. (THEOCHEM)* **1991**, *235*, 243–262.
- (26) Joly, H. A.; Howard, J. A.; Artega, G. A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 750–759.
- (27) Fängström, T.; Lunell, S.; Kasai, P. H.; Eriksson, L. A. *J. Phys. Chem. A* **1998**, *102*, 1005–1017.
- (28) Allouti, F.; Alikhani, M. E. *J. Mol. Struct. (THEOCHEM)* **2004**, *683*, 89–96.
- (29) Joly, H. A.; Brunet, F. D.; Feola, J. C. *J. Phys. Chem. A* **2012**, *116*, 2439–2452.
- (30) Knight, L. B., Jr.; Woodward, J. R.; Thomas, J. K.; Arrington, C. A. *J. Phys. Chem.* **1993**, *97*, 1304–1311.