

## Molecular Aluminium Trihydride, $\text{AlH}_3$ : Generation in a Solid Noble Gas Matrix and Characterisation by its Infrared Spectrum and *Ab Initio* Calculations

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Broad-band photolysis of a solid noble gas matrix containing Al atoms and  $\text{H}_2$  gives rise to the planar, monomeric  $\text{AlH}_3$  molecule, isotopically natural and deuteriated forms of which have been characterised by their IR spectra; confirmation is afforded by the results of MP2 *ab initio* and normal coordinate analysis calculations.

The synthesis and characterisation of the binary hydride of gallium,  $[\text{GaH}_3]_n$ ,<sup>1</sup> have stimulated renewed interest in the hydrides of the Group 13 metals.<sup>2</sup> The ensuing flurry of theoretical enquiries<sup>3</sup> has tended to underline the seemingly anomalous position of aluminium which gives an involatile polymeric hydride  $[\text{AlH}_3]_n$ ,<sup>4</sup> but only fleeting signs of discrete gaseous molecules like  $\text{AlH}_3$  and  $\text{Al}_2\text{H}_6$  (identified by mass spectrometry).<sup>5</sup> We have confirmed that evaporation of aluminium from a hot tungsten filament into a hydrogen atmosphere (*e.g.* at a pressure of 2–3 mmHg†) yields at 77 K a heterogeneous solid condensate including elemental aluminium and a hydride with the empirical composition  $\text{AlH}_x$ . Circumstantial evidence based on the overall composition of

the deposit implies that  $x > 1$ . Warming the deposit to ambient temperatures results in decomposition of  $\text{AlH}_x$  with the regeneration of  $\text{H}_2$ . Such decomposition can be forestalled, however, by chemical trapping with an excess of trimethylamine; warming then affords the known, relatively stable adduct  $(\text{Me}_3\text{N})_2\text{AlH}_3$  identified by its IR and  $^1\text{H}$  and  $^{27}\text{Al}$  NMR spectra.<sup>6</sup> Although this points to  $\text{AlH}_3$  as the precursor, the inhomogeneous nature of the condensate means that disproportionation cannot be ruled out as a pathway to  $(\text{Me}_3\text{N})_2\text{AlH}_3$ .

Matrix isolation is a well tried stratagem in this area.<sup>7</sup> Hence the monomeric gallane molecules  $\text{GaH}_x\text{Cl}_{3-x}$ , generated photolytically *via* the reactions of molecular  $\text{GaCl}$  with  $\text{HCl}$  ( $x = 1^{\text{8a}}$ ) or  $\text{H}_2$  ( $x = 2^{\text{8b}}$ ), have been characterised by their IR spectra. Likewise the binary hydride molecules  $\text{GaH}$ ,  $\text{Ga}_2\text{H}_2$  and  $\text{GaH}_2$  have been identified in cryogenic reactions invol-

† 1 mmHg  $\approx$  133 Pa.

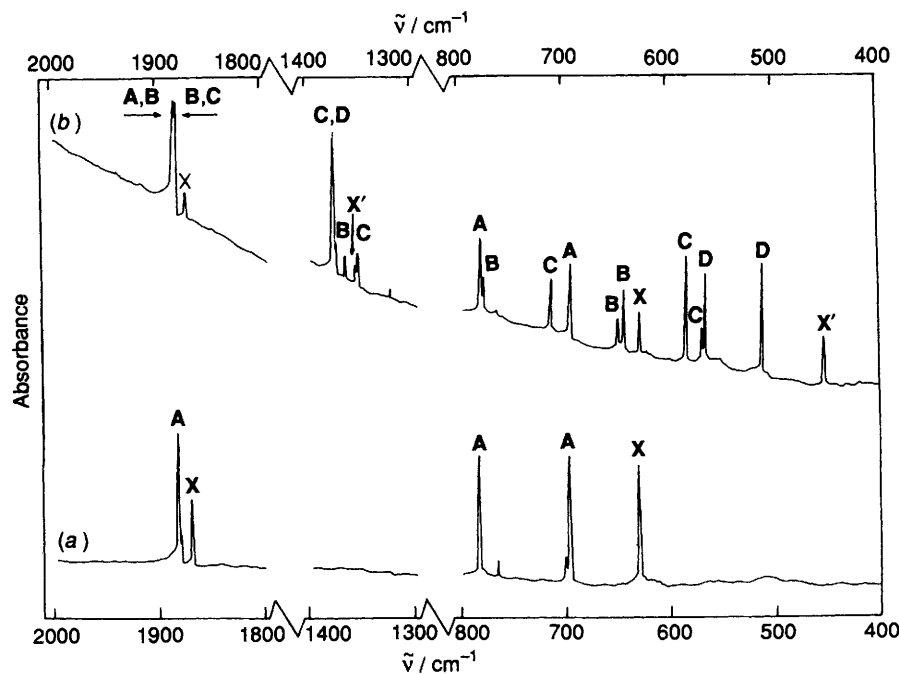


Fig. 1 IR spectra of Ar matrices containing Al atoms and  $\text{H}_2$  or  $\text{H}_2 + \text{D}_2$  showing the effects of broad-band photolysis: (a) Al with  $\text{H}_2$  after photolysis for 20 min; (b) Al with  $\text{H}_2 + \text{D}_2$  in 1:1 proportions after photolysis for 40 min. The species A, B, C and D are identified in Table 1. X and X' correspond to a hydride impurity and the corresponding deuteride, respectively (see footnote§).

ving  $\text{H}_2$  and Ga atoms or  $\text{Ga}_2$  molecules.<sup>9</sup> Photo-excitation of matrix-isolated Al atoms in the presence of  $\text{H}_2$  leads, it has been reported,<sup>10</sup> to the formation of the species  $\text{AlH}_2$  and  $\text{AlH}$ . We have carried out similar experiments in which Al vapour has been co-condensed with an excess of Ar or Kr containing ca. 5%  $\text{H}_2$ .<sup>‡</sup> The IR spectrum of the resulting matrix showed only weak absorptions associated with impurities, with no hint of features attributable to molecules containing Al–H bonds. However, exposure of the matrix to radiation spanning the wavelengths 200–800 nm for 10–40 min led to the appearance and growth of new IR bands (see Fig. 1). Most conspicuous were three bands occurring for an Ar matrix at 1882.7, 783.5 and 697.6  $\text{cm}^{-1}$ , the growth patterns of which left no doubt that they are carried by a single molecule A (the corresponding bands for a Kr matrix were at 1874.5, 777.7 and 690.4  $\text{cm}^{-1}$ ). The number and energies of the bands, allied to the precedents of earlier experiments, argue that A is an aluminium hydride, but not  $\text{AlH}$ ,  $\text{AlH}_2$  or  $\text{HAIOH}$ .<sup>10,12</sup>  $\text{AlH}$  may be present but its characteristic absorption (near 1590  $\text{cm}^{-1}$ ) would be obscured, at least partially, by features due either to  $\text{H}_2\text{O}$  impurity in the matrix or to atmospheric moisture.<sup>§</sup>

‡ Al was evaporated from a graphite vessel at ca. 1273 K and the vapours were condensed on a copper block cooled to ca. 16 K. The condensate was estimated typically to have a composition  $\text{Ar}(\text{Kr}) : \text{H}_2 : \text{Al}$  in the order of 1000:50:5. A Bruker IFS 66v FTIR spectrometer was used to measure the IR spectrum of the matrix in reflection and to monitor the effects of photolysis with the output of a medium-pressure mercury lamp; the resolution was typically 1  $\text{cm}^{-1}$ . Other experimental details have been described earlier.<sup>8a,11</sup>

§ Apart from weaker satellites accompanying the bands due to A and attributable to matrix site effects, there were only two other bands of significant intensity which also grew on photolysis. Occurring at 1870.6 (1357.7) and 631.1 (454.6)  $\text{cm}^{-1}$  in experiments with  $\text{H}_2$  ( $\text{D}_2$ ), as illustrated in Fig. 1, these were shown by control experiments to belong to an unidentified impurity X (X') whose formation proceeded independently of the presence of any aluminium in the graphite vessel. The experiments carried out so far clearly imply that X is a metal hydride molecule derived either from an impurity in the graphite itself or, more likely, from the reduction of some other component of the furnace by the hot graphite.

Given the conditions of the matrix experiments, the most plausible interpretation of the IR spectrum is that A is the elusive monomeric trihydride  $\text{AlH}_3$  with the expected trigonal planar structure conforming to  $D_{3h}$  symmetry. This identification we have endorsed (a) by examining the effects of replacing  $\text{H}_2$  by  $\text{D}_2$  or a mixture of  $\text{H}_2$  and  $\text{D}_2$ , and (b) by comparison of the experimental findings with the results of *ab initio* calculations.

(a) The perdeuterated version of the hydride, D, the dominant product of broad-band photolysis of an Ar matrix containing Al atoms and ca. 5%  $\text{D}_2$ , was observed to display an IR spectrum correlating with that of A. Shifts to substantially lower energies (1882.7  $\rightarrow$  1376.5, 783.5  $\rightarrow$  568.4 and 697.6  $\rightarrow$  513.9  $\text{cm}^{-1}$ ) evince large H(D) displacements for all three modes. Experiments with mixtures of  $\text{H}_2$  and  $\text{D}_2$  yielded no less than 15 IR absorptions attributable to A, D and mixed H/D isotopomers (see Fig. 1), 10 of these occurring in the region 500–800  $\text{cm}^{-1}$ . In addition, experiments including  $\text{D}_2$  as a reagent gave rise to an absorption at 1157.6  $\text{cm}^{-1}$  most obviously ascribed to  $\text{AlD}$ ,<sup>10,12</sup> as the bands due to A, D, etc. grew with continued broad-band photolysis, this feature was seen to decay.

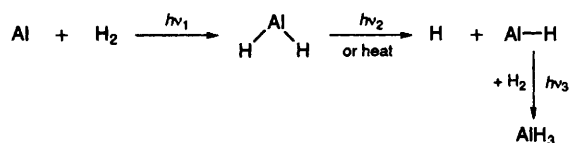
(b) Perhaps the most cogent evidence that A is  $\text{AlH}_3$  comes from the results of MP2 *ab initio* and normal coordinate analysis calculations.<sup>¶</sup> The *ab initio* analysis has yielded

¶ Program used: CADPAC 4.0 (MP2 geometry optimisations):<sup>13</sup> basis set quality TZ2P for H and Al; basis sets derived from refs. 14 and 15. Basis set parameters:  $\text{H}(5s2p)/[3s2p]\eta_d = 0.46$  and 1.39;  $\text{Al}(12s9p2d)/[7s5p2d]\eta_d = 0.17$  and 0.52. Total energy,  $E_{\text{tot}}^{\text{MP2}} = -243.827294$  hartrees. Optimised Al–H distance = 157.1 pm, *i.e.* appreciably shorter than that found in  $\text{AlH}$  (164.8 pm).<sup>12b</sup> Frequencies computed in this way are normally some 5% higher than  $\omega_e$  values determined experimentally which are in turn larger than observed, anharmonic frequencies, by up to ca. 60  $\text{cm}^{-1}$  for vibrations like  $\nu(\text{Al-H})$  with large amplitudes. The results of the normal coordinate analysis presented in Table 1 are based on the optimised structure deduced from the *ab initio* calculations. A harmonic force field was used with no more than four independently refined force constants; for all the in-plane fundamentals, the harmonic frequencies thus generated were converted to *anharmonic* frequencies by the empirical procedures described in ref. 16. Further details will be presented elsewhere.

**Table 1** Vibrational frequencies ( $\bar{\nu}$  in  $\text{cm}^{-1}$ ) for  $\text{AlH}_3$  (A),  $\text{AlH}_2\text{D}$  (B),  $\text{AlHD}_2$  (C) and  $\text{AlD}_3$  (D) (a) observed for the molecules isolated in Ar matrices, (b) calculated by the MP2 *ab initio* method and (c) calculated by normal coordinate analysis (n.c.a.)

Species	Experiment, Ar matrix	Assignment	Calculated	
			MP2 <i>ab initio</i> method (intensity) <sup>a</sup>	N.c.a. <sup>b</sup>
$\text{AlH}_3$ , A	1882.7	$\nu_{\text{as}}(\text{AlH}_2)$ ( $e'$ )	2024.2 (268)	1881.4
	N.o. <sup>c</sup>	$\nu_{\text{s}}(\text{AlH}_3)$ ( $a_1'$ )	2021.0 (0)	1880.6
	783.5	$\delta(\text{AlH}_2)$ ( $e'$ )	830.7 (249)	782.5
	697.6	$\gamma(\text{AlH}_3)$ ( $a_2''$ )	737.6 (394)	697.8 <sup>d</sup>
$\text{AlH}_2\text{D}$ , B	1882.7	$\nu_{\text{as}}(\text{AlH}_2)$ ( $b_2$ )	2024.1 (271)	1881.3
	1881.2	$\nu_{\text{s}}(\text{AlH}_2)$ ( $a_1$ )	2022.1 (93)	1880.9
	1367.3	$\nu(\text{AlD})$ ( $a_1$ )	1455.6 (99)	1366.8
	780.6	$\delta(\text{AlH}_2)$ ( $a_1$ )	830.4 (246)	782.2
	651.8	$\rho(\text{AlD})$ ( $b_2$ )	687.0 (170)	649.3
	645.6	$\gamma(\text{AlH}_2\text{D})$ ( $b_1$ )	680.2 (335)	643.4 <sup>d</sup>
$\text{AlHD}_2$ , C	1881.2	$\nu(\text{AlH})$ ( $a_1$ )	2023.0 (186)	1881.0
	1377.9	$\nu_{\text{as}}(\text{AlD}_2)$ ( $b_2$ )	1468.4 (155)	1378.0
	1355.2	$\nu_{\text{s}}(\text{AlD}_2)$ ( $a_1$ )	1442.6 (49)	1355.6
	716.4	$\rho(\text{AlH})$ ( $b_2$ )	761.6 (206)	717.4
	586.7	$\gamma(\text{AlHD}_2)$ ( $b_1$ )	617.4 (276)	584.0 <sup>d</sup>
	570.8	$\delta(\text{AlD}_2)$ ( $a_1$ )	601.9 (130)	570.1
$\text{AlD}_3$ , D	1376.5	$\nu_{\text{as}}(\text{AlD}_2)$ ( $e'$ )	1468.4 (155)	1378.0
	N.o. <sup>c</sup>	$\nu_{\text{s}}(\text{AlD}_3)$ ( $a_1'$ )	1429.7 (0)	1344.4
	568.4	$\delta(\text{AlD}_2)$ ( $e'$ )	601.2 (128)	569.5
	513.9	$\gamma(\text{AlD}_3)$ ( $a_2''$ )	547.4 (217)	517.8 <sup>d</sup>

<sup>a</sup> Intensities in  $\text{km mol}^{-1}$ , as obtained from the frequency calculation. For direct comparison with observed intensities, these values need to be scaled according to the probabilities of formation of the different  $\text{AlH}_n\text{D}_{3-n}$  isotopomers in matrices containing both  $\text{H}_2$  and  $\text{D}_2$ . <sup>b</sup> See footnote  $\ddagger$ . <sup>c</sup> N.o. not observed. Fundamental is silent in IR absorption for an  $\text{AlH}_3$  or  $\text{AlD}_3$  molecule with  $D_{3h}$  symmetry. <sup>d</sup> Harmonic frequency for the out-of-plane deformation; in fact, this mode shows evidence of a negative anharmonicity term, a feature also conspicuous in the corresponding mode of the planar  $\text{CH}_3$  radical.<sup>17</sup>



**Scheme 1**

frequencies and intensities for all the fundamentals of the molecules  $\text{AlH}_3$ ,  $\text{AlH}_2\text{D}$ ,  $\text{AlHD}_2$  and  $\text{AlD}_3$ . The results are in excellent agreement with the findings of other theoretical investigations.<sup>3b</sup> The frequency and intensity patterns offer a more-or-less incontrovertible basis for interpreting the IR spectra of the normal and deuterated forms of A. We can account for the doublet structure of the absorption near  $1880 \text{ cm}^{-1}$  and the three absorptions occurring in the region  $1350\text{--}1380 \text{ cm}^{-1}$  in the spectrum of a photolysed matrix containing both  $\text{H}_2$  and  $\text{D}_2$  (see Fig. 1 and Table 1). Here some of the relevant (bond-stretching) fundamentals of different  $\text{AlH}_n\text{D}_{3-n}$  isotopomers are coincident or nearly so. This situation does not arise, however, with the bending modes, and no aspect of the analysis is more telling than the prediction and observation of just 10 distinct vibrational modes in the region  $500\text{--}800 \text{ cm}^{-1}$ .

Our experiments disclose, then, the formation of  $\text{AlH}_3$  on broad-band photolysis of Al atoms in an  $\text{H}_2$ -doped noble gas matrix.  $\text{AlH}$  appears to be an intermediate, but of the  $\text{AlH}_2$  previously reported<sup>10</sup> there was little or no sign, possibly through our use (i) of broad- rather than narrow-band conditions of photolysis, and (ii) of matrices relatively richer in  $\text{H}_2$ . That an equimolar mixture of  $\text{H}_2$  and  $\text{D}_2$  gives  $\text{AlH}_3$ ,

$\text{AlH}_2\text{D}$ ,  $\text{AlHD}_2$  and  $\text{AlD}_3$  in highly non-statistical proportions approaching 1 : 1 : 1 : 1 favours the mechanism in Scheme 1 in which the ultimate step parallels the oxidative addition of  $\text{H}_2$  to  $\text{GaCl}$ .<sup>8b</sup> Preliminary annealing experiments (at temperatures up to 26 K in a Kr matrix) resulted only in the decay of all the product bands, with no signs signalling concomitant formation of  $\text{Al}_2\text{H}_6$ , but this may reflect merely the low concentrations of the  $\text{AlH}_3$  in the experiments carried out so far. In this and other respects there is much still to be learnt about  $\text{AlH}_3$ , and further experiments in our laboratories are now in progress.

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