

**681.** *The Vibrational Spectrum of  $\text{AlH}_3 \cdot 2\text{NMe}_3$ .*

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A normal co-ordinate analysis of  $\text{AlH}_3 \cdot 2\text{NMe}_3$  has been carried out on the basis of  $D_{3h}$  symmetry. From calculations based on a simple valence force field approximation for the  $a_1'$  and  $a_2''$  modes it is suggested that previous assignments of "aluminium-nitrogen stretching vibrations" are in error. Although the molecular oscillators suffer only mechanical (G-matrix) coupling in this approximation, the results demonstrate the dangers inherent in assigning a frequency to the stretching of a particular bond rather than to a mode of vibration of the whole molecule.

"METAL-NITROGEN stretching vibrations" in co-ordination compounds of amines and ammonia have long been of interest, but progress in making unambiguous assignments has been slow. Recently, two important Papers appeared<sup>1,2</sup> describing the use of Raman and infrared techniques to study trimethylamine addition compounds of  $\text{AlH}_3$  and  $\text{AlD}_3$ . Both sets of authors report similar frequencies in the spectra of the various compounds. In particular, their assignments for the 1 : 2 adducts are in agreement. N-Al-N stretching

<sup>1</sup> Fraser, Greenwood, and Straughan, *J.*, 1963, 3744.

<sup>2</sup> Heitsch and Kniseley, *Spectrochim. Acta*, 1963, **19**, 1385.

modes are assigned at 461 (ref. 1) and 466 (ref. 2)  $\text{cm}^{-1}$  (symmetric), and at 460 (refs. 1 and 2)  $\text{cm}^{-1}$  (antisymmetric), in  $\text{AlH}_3\cdot 2\text{NMe}_3$  and its  $\text{AlD}_3$  analogue. On inspection, coincidence of these frequencies is unlikely, and it was this observation which led us to carry out the calculations reported here. One mode ( $a_1'$ ) involves no movement of the aluminium, whereas the other (antisymmetric) stretching mode ( $a_2''$ ) does involve movement of this (light) atom.

Assuming a linear N–Al–N grouping,<sup>3</sup> the possible symmetries for the molecular species  $\text{AlH}_3\cdot 2\text{NMe}_3$ , with methyl as a point mass, are  $D_{3h}$ ,  $C_{3h}$ ,  $D_3$ ,  $C_{3v}$ , and  $C_3$ . The number of vibrational modes of each symmetry class together with their activities are given

TABLE 1.  
Vibrational modes and activities for  $\text{AlH}_3\cdot 2\text{NMe}_3$ .

$D_{3h}$	$C_{3h}$	$D_3$	$C_{3v}$	$C_3$
$4a_1'$ (Raman)	$5a'$ (Raman)	$5a_1$ (Raman)	$8a_1$ (i.r. and R)	$10a$ (i.r. and R)
$1a_1''$ (inactive)	$5a_2''$ (i.r.)	$5a_2$ (i.r.)	$2a_2$ (inactive)	
$1a_2'$ (inactive)				
$4a_2''$ (i.r.)				
$6e'$ (i.r. and R)	$6e'$ (i.r. and R)	$10e$ (i.r. and R)	$10e$ (i.r. and R)	$10e$ (i.r. and R)
$4e''$ (R)	$4e''$ (R)			

in Table 1. Chemically, the most likely model is that based on  $D_{3h}$ , although Heitsch and Kniseley<sup>2</sup> suggest  $D_3$  on the basis of the infrared activity of the N–Al–H deformation mode. To reduce the number of force constants that it is necessary to assume, we carried out a normal co-ordinate analysis (using the standard Wilson F–G matrix technique), assuming  $D_{3h}$  symmetry and with the simple valence force field (SVFF) approximation. The symmetry co-ordinates used in this analysis, together with the resultant F and G matrix elements, are given in the Appendix. In the analysis, general ( $D_{3h}$ ) angles were used, but in the calculations the tetrahedral approximation was introduced. Mostly deformational constants are involved in the  $e$ -type secular equations, so that we have not attempted any calculations on these modes. However, even allowing for our lack of knowledge of force constants in such molecules, it is possible to make some useful predictions for the non-degenerate vibrations. Table 2 shows computed values of the vibrational frequencies ( $a_1'$  and  $a_2''$ ) for  $\text{AlH}_3\cdot 2\text{NMe}_3$ , using an N–C stretching force constant of  $4 \times 10^5$  dynes  $\text{cm}^{-1}$ . The deformational constants were estimated on the basis of the mean of one tenth of the adjacent bond stretches, giving values of  $F_{33}$  (=  $F_{77}$ ) in the range 0.7–1 millidyne  $\text{\AA}$  radian<sup>-2</sup> for an aluminium–nitrogen force constant of  $1\text{--}2 \times 10^5$  dynes  $\text{cm}^{-1}$ . The value for  $F_{88}$  was taken to be 0.4–0.6 millidyne  $\text{\AA}$  radian<sup>-2</sup>. Relevant potential energy contributions to the various normal modes are also given in Table 2. It should be noted that, as we have used the SVFF approximation, and as the aluminium does not move in  $a_1'$  vibrations, this Al–H stretching mode cannot couple with other vibrations of the same symmetry (in our calculations). Hence, there are only three frequencies reported under  $a_1'$ , but four under  $a_2''$ . The  $a_1'$  mode corresponding to the  $\text{AlH}_3$  “breathing frequency” was used to calculate the Al–H stretching force constant.

Heitsch and Kniseley<sup>2</sup> point out that there is no “discernible perturbation” of the spectrum of trimethylamine on co-ordination to  $\text{AlH}_3$  to give the 2 : 1 adduct. By analogy with work on related adducts,<sup>4</sup> such as  $\text{NMe}_3\cdot\text{TiCl}_4$ , this would be surprising even for an Al–N stretching force constant as low as *ca.*  $10^5$  dynes  $\text{cm}^{-1}$ . However, it is possible that the trimethylamine present (it is due to dissociation of the adduct to give the 1 : 1 compound) may have made identification of co-ordinated trimethylamine somewhat difficult. The results in Table 2 show that for a force constant of about  $10^5$  dynes  $\text{cm}^{-1}$  a mode at about 150  $\text{cm}^{-1}$  can be identified with the totally symmetric Raman-active Al–N stretching mode. Increasing the force constant of this bond to  $2 \times 10^5$  dynes  $\text{cm}^{-1}$  makes the

<sup>3</sup> Heitsch, Nordman, and Parry, *Inorg. Chem.*, 1963, **2**, 508.

<sup>4</sup> Beattie and Gilson, unpublished work.

TABLE 2.

Calculated vibrational frequencies of  $\text{AlH}_3\cdot 2\text{NMe}_3$ , including contributions to the potential-energy (P.E.) function.

Stretch, and deform. consts.*			Fre- quency ( $\text{cm.}^{-1}$ ) $a_1'$	P.E. contributions (%)			Fre- quency ( $\text{cm.}^{-1}$ ) $a_2''$	P.E. contributions (%)				
Al-N str.	NMe def.	$\text{AlH}_3$ o.p. def. ( $a_2''$ only)		Al-N str.	NMe str.	NMe def.		Al-N str.	NMe str.	NMe def.	$\text{AlH}_3$ o.p. def.	
1	1	0.4	908	9	61	30	917	13	56	29	2	
			540	9	39	52	774	2	3	0	95	
			154	82	0	18	551	16	41	41	1	
		0.6	330				917	69	0	29	2	
			957				899	7	8	5	80	
			552				552	17	41	41	0	
	1	0.7	0.4	871	9	73	19	882	14	65	18	3
				487	16	27	57	774	1	5	0	93
				149	75	0	24	509	31	30	38	2
			0.6	311				311	54	0	44	2
				952				952	5	3	1	92
				873				873	9	67	17	6
2	1	0.4	951	19	51	30	990	33	38	26	3	
			563	14	49	38	780	2	9	2	87	
			200	67	0	32	595	27	52	15	7	
		0.6	396				396	38	1	58	3	
			1012				1012	29	23	16	32	
			922				922	3	22	11	64	
	2	0.7	0.4	600				600	30	55	13	2
				398				398	38	1	59	2
				910	19	61	20	954	36	43	17	5
			0.6	524	24	38	38	778	2	13	1	84
				187	57	0	42	584	38	43	10	9
				353				353	25	1	72	2
2	0.7	0.4	993				993	25	16	7	53	
			904				904	9	36	11	43	
			589				589	41	47	9	3	
		0.6	353				353	25	1	73	1	

\*  $10^5$  dynes  $\text{cm.}^{-1}$  or mdynes  $\text{\AA}$  radian $^{-2}$ . Distances: N-Me 1.47, N-Al 2.16, Al-H 1.6  $\text{\AA}$ .

identification of an Al-N stretching frequency less unambiguous, but a mode at about  $190 \text{ cm.}^{-1}$  is largely the Al-N symmetric stretch. A band at  $197 \text{ cm.}^{-1}$  in the Raman spectrum of  $\text{AlH}_3\cdot 2\text{NMe}_3$ , and assigned to an Al-N deformation, is probably the one calculated by us to be about 70% N-Al-N stretch. The antisymmetric N-Al-N stretching mode is even more difficult to discuss, as coupling here is more marked. With a force constant of  $2 \times 10^5$  dynes  $\text{cm.}^{-1}$  it is impossible to talk meaningfully of an aluminium-nitrogen antisymmetric stretching mode. However, all the frequencies recorded for the  $a_2''$  modes are higher than that assigned as an Al-N stretching mode under  $a_1'$ . Coupling with  $\text{AlH}_3$  out-of-plane deformation for  $a_2''$  species is difficult to predict but can, even in the extreme approximation we have considered, be serious. A particular case occurs for the force constant sequence 2, 0.7, 0.6, where there is considerable mixing with other vibrations. Finally, even with an Al-N force constant of  $3 \times 10^5$  dynes  $\text{cm.}^{-1}$  the general picture is similar to that outlined here.

We conclude by pointing out that it is probable that the vibrations around  $460 \text{ cm.}^{-1}$ , which are active in both the infrared and the Raman effect, are  $e$ -type modes. We find<sup>4</sup> that with many adducts of trimethylamine (*e.g.*,  $\text{NMe}_3\cdot\text{TiCl}_4$  436;  $\text{NMe}_3\cdot\text{GeCl}_4$  435;  $\text{NMe}_3\cdot\text{SnCl}_4$  426  $\text{cm.}^{-1}$ ) there is an infrared frequency around  $460 \text{ cm.}^{-1}$ . Assignments on

a complicated molecule such as  $\text{AlH}_3\cdot 2\text{NMe}_3$  are almost always open to criticism. Our elementary calculations are equally open to criticism, but do have the advantage of indicating how serious the problem is likely to be for co-ordination compounds in general. This does not mean that chemists should not continue to look at co-ordination compounds of this type, but rather that detailed studies of the infrared and Raman spectra (including isotopic substitution and polarization data) of compounds of known stereochemistry are necessary to enable force constants obtained for these molecules to assist in the assignment of force constants to molecules of unknown structure.

## APPENDIX

*Symmetry co-ordinates for  $\text{AlH}_3\cdot 2\text{NMe}_3$  (methyl taken as a point mass; point group  $D_{3h}$ ). N.B.  $n = (\sqrt{3} \cos \beta) / \cos(\alpha/2)$ .*

$$a_1' S_1 = (1/\sqrt{2})(\Delta r_1 + \Delta r_2);$$

$$S_2 = (1/\sqrt{6})(\Delta R_1 + \Delta R_2 + \Delta R_3 + \Delta R_4 + \Delta R_5 + \Delta R_6);$$

$$S_3 = [1/\sqrt{6(1+n^2)}][\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6 + n(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{23} + \Delta\alpha_{45} + \Delta\alpha_{46} + \Delta\alpha_{56})];$$

$$S_4 = (1/\sqrt{3})(\Delta d_1 + \Delta d_2 + \Delta d_3).$$

( $S_4$  is entirely uncoupled in the G-matrix.)

$$a_2'' S_5 = (1/\sqrt{2})(\Delta r_1 - \Delta r_2);$$

$$S_6 = (1/\sqrt{6})[\Delta R_1 + \Delta R_2 + \Delta R_3 - (\Delta R_4 + \Delta R_5 + \Delta R_6)];$$

$$S_7 = [1/\sqrt{6(1+n^2)}][\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 - (\Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6) + n(\Delta\alpha_{12} + \Delta\alpha_{13} + \Delta\alpha_{23}) - n(\Delta\alpha_{45} + \Delta\alpha_{46} + \Delta\alpha_{56})];$$

$$S_8 = (1/\sqrt{6})[\Delta\epsilon_{1a} + \Delta\epsilon_{2a} + \Delta\epsilon_{3a} - (\Delta\epsilon_{1b} + \Delta\epsilon_{2b} + \Delta\epsilon_{3b})];$$

$$e' S_{9a} = (1/2\sqrt{3})[2\Delta R_1 - (\Delta R_2 + \Delta R_3) + 2\Delta R_4 - (\Delta R_5 + \Delta R_6)];$$

$$S_{10a}^* = (2/\sqrt{7})[\Delta\gamma_a + \frac{1}{2}(\Delta\epsilon_{1a} + \Delta\epsilon_{1b}) - \frac{1}{2}(\Delta\epsilon_{2a} + \Delta\epsilon_{2b} + \Delta\epsilon_{3a} + \Delta\epsilon_{3b})];$$

$$S_{11a} = (1/2\sqrt{3})[2\Delta\beta_1 - (\Delta\beta_2 + \Delta\beta_3) + 2\Delta\beta_4 - (\Delta\beta_5 + \Delta\beta_6)];$$

$$S_{12a} = (1/2\sqrt{3})[2\Delta\alpha_{23} - (\Delta\alpha_{12} + \Delta\alpha_{13}) + 2\Delta\alpha_{56} - (\Delta\alpha_{45} + \Delta\alpha_{46})];$$

$$S_{13a} = (1/\sqrt{6})[2\Delta d_1 - (\Delta d_2 + \Delta d_3)];$$

$$S_{14a} = (1/\sqrt{6})[2\Delta\theta_1 - (\Delta\theta_2 + \Delta\theta_3)];$$

$$e'' S_{15a} = (1/2\sqrt{3})[2\Delta R_1 - (\Delta R_2 + \Delta R_3) - 2\Delta R_4 + (\Delta R_5 + \Delta R_6)];$$

$$S_{16a} = (1/2\sqrt{3})[2\Delta\beta_1 - (\Delta\beta_2 + \Delta\beta_3) - 2\Delta\beta_4 + (\Delta\beta_5 + \Delta\beta_6)];$$

$$S_{17a} = (1/2\sqrt{3})[2\Delta\alpha_{23} - (\Delta\alpha_{12} + \Delta\alpha_{13}) - 2\Delta\alpha_{56} + (\Delta\alpha_{45} + \Delta\alpha_{46})];$$

$$S_{18a} = (1/\sqrt{3})[\Delta\epsilon_{1a} - \Delta\epsilon_{1b} + \frac{1}{2}(\Delta\epsilon_{2b} - \Delta\epsilon_{2a} + \Delta\epsilon_{3b} - \Delta\epsilon_{3a})].$$

The resultant F and G matrix elements are:

$$a_1' F_{11} = f_r; F_{22} = f_R; F_{33} = [1/(1+n^2)](f_\beta + n^2 f_\alpha); F_{44} = f_d; G_{11} = \mu_N;$$

$$G_{12} = -\sqrt{3}\mu_N \cos \beta; G_{13} = \sqrt{3}(1+n^2)(\mu_N/R) \sin \beta; G_{14} = 0; G_{22} = \mu_{Me} + 3\mu_N \cos^2 \beta;$$

$$G_{23} = -3\sqrt{(1+n^2)}(\mu_N/R) \cos \beta \sin \beta; G_{24} = 0; G_{33} = [(1+n^2)/R^2](\mu_{Me} + 3\mu_N \sin^2 \beta);$$

$$G_{34} = 0; G_{44} = \mu_H.$$

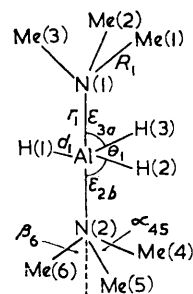
In SVFF the F and G matrices may be reduced by removal of  $F_{44}$  and  $G_{44}$ , leaving a  $3 \times 3$  matrix in each case.

$$a_2'' F_{55} = F_{11}; F_{66} = F_{22}; F_{77} = F_{33}; F_{88} = f_\epsilon; G_{55} = 2\mu_{Al} + \mu_N; G_{56} = G_{12}; G_{57} = G_{13};$$

$$G_{58} = -(2\sqrt{3}/d)\mu_{Al}; G_{66} = G_{22}; G_{67} = G_{23}; G_{68} = 0; G_{77} = G_{33}; G_{78} = 0;$$

$$G_{88} = (2/d^2)(3\mu_{Al} + \mu_H).$$

\* The  $\Delta\gamma_a$  refers to bending the N-Al-N system, and  $\gamma_a$  is technically a redundant co-ordinate. We have adopted the unorthodox retention of this co-ordinate because of its possible assistance in discussing this deformation of the molecule.



$$\begin{aligned}
e' \quad F_{99} &= f_R; \quad F_{10,10} = (4/7)(f_\gamma + 3f_\epsilon/4); \quad F_{11,11} = f_\beta; \quad F_{12,12} = f_\alpha; \quad F_{13,13} = f_d; \quad F_{14,14} = f_\theta; \\
G_{99} &= \mu_{Me} + (3/2)\sin^2 \beta \mu_N; \quad G_{9,10} = -(\sqrt{21/2r})\sin \beta \mu_N; \quad G_{9,11} = (3/2)(1/r + \cos \beta/R)\sin \beta \mu_N; \\
G_{9,12} &= (3/2)(m/R)\sin \beta \mu_N; \quad G_{9,13} = 0; \quad G_{9,14} = 0; \quad G_{10,10} = (7/r^2)\mu_{Al} + (7/2r^2)\mu_N; \\
G_{10,11} &= -(\sqrt{21/r^2})\mu_{Al} - (\sqrt{21/2r})(1/r + \cos \beta/R)\mu_N; \quad G_{10,12} = -(\sqrt{21/2r}R)m\mu_N; \\
G_{10,13} &= -(\sqrt{21/\sqrt{2r}})\mu_{Al}; \quad G_{10,14} = -(3\sqrt{7/\sqrt{2d}})\mu_{Al}; \\
G_{11,11} &= (\mu_{Me}/R^2) + (3/r^2)\mu_{Al} + (3/2)(1/r + \cos \beta/R)^2\mu_N; \\
G_{11,12} &= -(n/2R^2)\mu_{Me} + (3/2)(m/R)(1/r + \cos \beta/R)\mu_N; \quad G_{11,13} = (3/\sqrt{2r})\mu_{Al}; \\
G_{11,14} &= (3\sqrt{3/\sqrt{2rd}})\mu_{Al}; \quad G_{12,12} = (\mu_{Me}/R^2)(3/p^2 + n^2/4) + (3/2)(m^2/R^2)\mu_N; \quad G_{12,13} = 0; \\
G_{12,14} &= 0; \quad G_{13,13} = (3/2)\mu_{Al} + \mu_H; \quad G_{13,14} = (3\sqrt{3/2d})\mu_{Al}; \quad G_{14,14} = (9/2)(\mu_{Al}/d^2) + 3\mu_H/d^2. \\
e'' \quad F_{15,15} &= f_R; \quad F_{16,16} = f_\beta; \quad F_{17,17} = f_\alpha; \quad F_{18,18} = f_\epsilon; \quad G_{15,15} = G_{99}; \quad G_{15,16} = G_{9,11}; \\
G_{15,17} &= G_{9,12}; \quad G_{15,18} = -(3/2r)\sin \beta \mu_N; \quad G_{16,16} = (\mu_{Me}/R^2) + (3/2)(1/r + \cos \beta/R)^2\mu_N; \\
G_{16,17} &= G_{11,12}; \quad G_{16,18} = -(3/2r)(1/r + \cos \beta/R)\mu_N; \quad G_{17,17} = G_{12,12}; \quad G_{17,18} = -(3m/2rR)\mu_N; \\
G_{18,18} &= (2/d^2)\mu_H + (3/2r^2)\mu_N; \quad m = \sin \beta \tan(\alpha/2); \quad n = \sqrt{3} \cos \beta / \cos(\alpha/2); \quad p = 2 \cos(\alpha/2).
\end{aligned}$$

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