Vibrational Spectra and Normal Coordinate Calculations for Trimethylaluminium-Ammonia

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Studies were carried out on the infrared spectra (33—4000 cm^{-1}) of four isotopic trimethylaluminium–ammonia complexes, $(CH_3)_3AlNH_3$, $(CD_3)_3AlNH_3$, $(CH_3)_3AlND_3$, and $(CD_3)_3AlND_3$, in the solid state at low temperature, and on the Raman spectra (0—4000 cm^{-1}) in the solid state and in solution of dichloromethane and of benzene at ambient temperature. Assignments for all fundamentals except internal torsion were made on the basis of C_{3v} molecular symmetry. For the sake of confirmation normal coordinate calculations were carried out utilizing a symmetry force field. The Al–N stretching force constant was found to be 1.544 mdyn/Å.

Numerous vibrational studies have been made on the coordination complexes of boron compounds with derivatives of the Group Vb elements. However, few studies are known for the addition complexes of aluminium compounds,[1–5] belonging to the same group as that of boron.

The present study was undertaken to observe the vibrational spectra of trimethylaluminium–ammonia complexes, to assign vibrational fundamentals and to calculate force constants, especially that of the Al–N bond. Complete vibrational analyses for these complexes might provide interesting information on the electron donor-acceptor bond, which in turn can be compared with other physical and chemical properties.

Experimental

All manipulation of chemical substances was done in the conventional vacuum line, because of inflammability of trimethylaluminium and sensitivity of the addition complexes to moisture.

Trimethylaluminium was prepared by the reaction of dimethylmercury(II) with aluminium powder in slight excess in a sealed tube with a break-seal, following the procedure of Wartik and Schlesinger.[6] Dimethyl-d_6-mercury(II) was used for the preparation of trimethylaluminium-d_9. Ammonia generated by dropping commercial aqueous ammonia over solid potassium hydroxide was collected in a U-type trap immersed in liquid nitrogen. Ammonia-d_3 was prepared by the reaction of deuterium oxide with magnesium nitride[7] in the vacuum line. These substances were purified by fractional distillation in the vacuum line.

Trimethylaluminium–ammonia complex for infrared work was prepared by condensing trimethylaluminium and ammonia in a 1:2 mole ratio into a small reaction tube with a stopcock and a ground-joint at liquid nitrogen temperature. After closing the stopcock the tube was left to reach room temperature. It was then opened to the vacuum line for a while in order to remove volatile substances.

The aluminium content was determined by the EDTA method.[8] Calcd for $(CH_3)_3AlNH_3$: Al, 30.3%. Found: Al, 29.3%.

Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer in the region 4000—400 cm^{-1}. Frequencies were read on a Hitachi QPD-33 recorder by abscissa expansion with use of a Perkin-Elmer Expanded Scale Readout Kit. The instrument was calibrated in the usual manner.[9] The spectra were obtained for the samples deposited onto a CsI plate cooled with liquid nitrogen. Before recording the spectra, the samples were annealed until the spectra showed no change.

Far infrared spectra were obtained between 400 and 33 cm^{-1} with a Hitachi FIS-III spectrophotometer which was evacuated in order to remove atmospheric water vapor. The instrument was calibrated by means of water vapor frequencies. The sample was sublimed onto a polyethylene window cooled with liquid nitrogen, and annealed in a similar manner to that for the midinfrared study. The double chopping method was used for recording the spectra to avoid the radiation effect resulting from the temperature difference between the sample and the reference beam path.

Raman spectra were recorded in the range 0—4000 cm^{-1} on a JEOL JRS-S1 laser Raman spectrophotometer equipped with an NEC GLG-108 50 mW He-Ne laser. The spectrophotometer was calibrated with the emmission lines of neon. The spectra were obtained at ambient temperature in the solid state and in the saturated solution of dichloromethane and of benzene, sealed in a capillary of about 1.5 mm o.d.

Results and Vibrational Assignments

The infrared and Raman spectra of four isotopic trimethylaluminium–ammonia complexes are shown in Figs. 1—3. The vibrational frequencies are given in Tables 1—4. A molecular symmetry of C_{3v}, with the C_3 axis coinciding with the Al–N bond, is assumed for trimethylaluminium–ammonia. From group theory, the molecule is expected to have $10A_1$, $5A_2$, and $15E$ modes, in which the A_2 mode is inactive in both the infrared and Raman spectra, and the A_1 and E modes are active in both.

CH_3 and CD_3 Modes. The CH_3 stretches are observed around 2900 cm^{-1} in the infrared spectra. The three asymmetric stretches are contained within a single intense absorption at 2910 cm^{-1} for $(CH_3)_3AlNH_3$ and at 2915 cm^{-1} for $(CH_3)_3AlND_3$. On deuteration of the methyl groups these stretches shift and split into two at 2184 and 2179 cm^{-1} for the NH_3 adduct, and at 2184 and 2177 cm^{-1} for the ND_3 adduct. The two symmetric methyl stretches are observed to be accidentally degenerate at 2874 cm^{-1} for $(CH_3)_3AlNH_3$ and at 2872 cm^{-1} for $(CH_3)_3AlND_3$, the modes shifting to 2089 cm^{-1} and to 2090 cm^{-1} on deuteration of the

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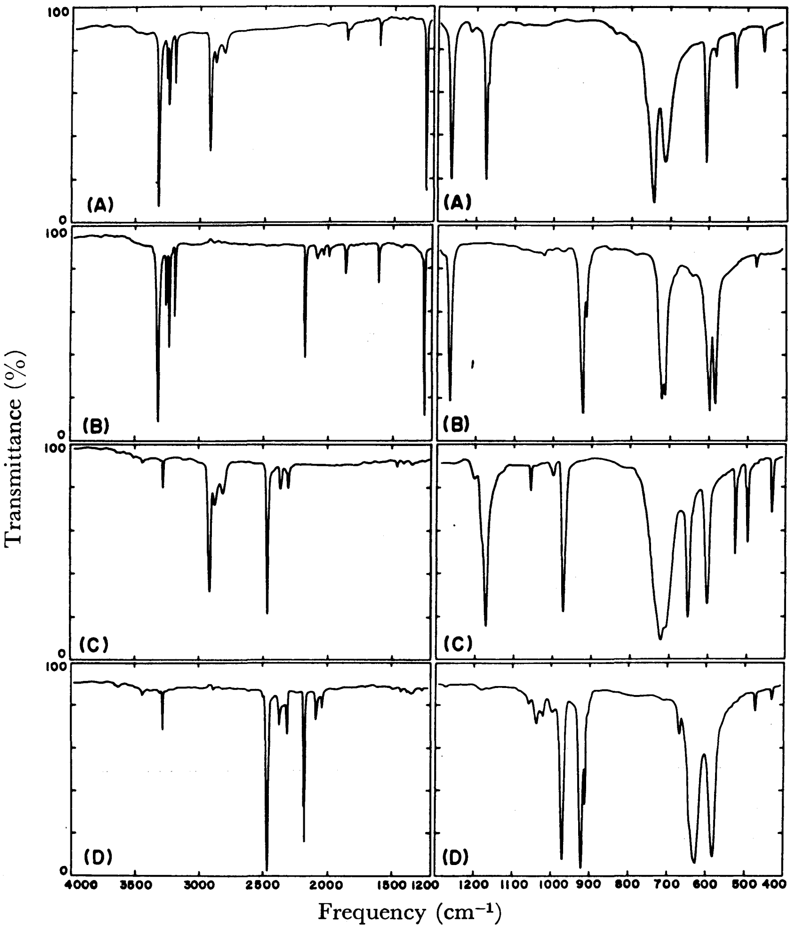

Fig. 1. Infrared spectra of (A) $(CH_3)_3AlNH_3$, (B) $(CD_3)_3AlNH_3$, (C) $(CH_3)_3AlND_3$, and (D) $(CD_3)_3$ $AlND_3$ recorded at −196 °C.

methyl groups. The Raman bands corresponding to the lower frequency infrared absorptions are polarized.

Degenerate methyl deformation is observed very weakly and broadly around 1470 and 1410 cm^{-1} in the infrared spectra. The frequencies are not definite, whereas the modes of $(CD_3)_3AlND_3$ are observed at 1038 cm^{-1} (ν_{21}) and 1021 cm^{-1} (ν_4 and ν_{22}). The deformation of $(CD_3)_3AlNH_3$ is too weak for the frequency to be defined.

Symmetric methyl deformation is observed as a singlet at 1172 cm^{-1} for $(CH_3)_3AlNH_3$ and at 1173 cm^{-1} for $(CH_3)_3AlND_3$. In the Raman spectra, the modes are observed at 1163 cm^{-1} and at 1165 cm^{-1} with a shoulder on the high-frequency side, the higher frequency bands being polarized. Consequently the 1172 and 1173 cm^{-1} infrared absorptions are assigned to the symmetric methyl deformation of A_1 symmetry, and the 1163 and 1165 cm^{-1} Raman bands, of E symmetry. The CD_3 modes are observed in the infrared spectra at 914 and 923 cm^{-1} for $(CD_3)_3AlNH_3$, and at 913 and 921 cm^{-1} for $(CD_3)_3AlND_3$, the lower frequency absorptions of which are weak. The Raman bands corresponding to the lower frequency infrared absorptions are strong and polarized.

The CH_3 rocks are assigned to absorptions at 743 cm^{-1} (ν_{25} and ν_{26}) and 712 cm^{-1} (ν_7) for $(CH_3)_3AlNH_3$, and at 720 cm^{-1} (ν_{25}) and 710 cm^{-1} (ν_7 and ν_{26}) for $(CH_3)_3AlND_3$. The CD_3 rocks are observed at 586 and 584 cm^{-1} in the infrared spectra for $(CD_3)_3AlNH_3$ and $(CD_3)_3AlND_3$, respectively, without splitting.

NH_3 and ND_3 Modes. The symmetric NH_3 stretch is assigned to an infrared absorption observed at 3254 cm^{-1} for the $(CH_3)_3Al$ and at 3252 cm^{-1} for the $(CD_3)_3Al$ adduct. On deuteration, the mode shifts from 3254 to 2369 cm^{-1} and from 3252 to 2373 cm^{-1}. The corresponding Raman bands are clearly polarized, though observed only weakly because of insufficient sensitivity of a photomultiplier in this region. The degenerate stretches are assigned to the most intense absorptions of these regions observed at 3313, 3312, 2463, and 2468 cm^{-1} for trimethylaluminium–ammonia-d_0, -d_9, -d_3, and -d_{12}, respectively.

The degenerate NH_3 deformation is observed at 1615 and 1618 cm^{-1} in the infrared spectrum for $(CH_3)_3$-$AlNH_3$ and $(CD_3)_3AlNH_3$, respectively. The ND_3 deformation shows no clear band in the infrared and Raman spectra, being observed at 1180 cm^{-1} as a shoulder on the high-frequency side of the symmetric CH_3 deformation or an extremely weak band in the infrared spectrum.

The symmetric NH_3 deformation is assigned to a band at 1263 and 1265 cm^{-1} in the infrared spectrum for $(CH_3)_3AlNH_3$ and $(CD_3)_3AlNH_3$, respectively. It shifts to 974 and 971 cm^{-1} on deuteration of the ammonia

Table 1. Observed and calculated frequencies (cm^{-1}) for $(CH_3)_3AlNH_3$[a]

No.[b]	Infrared Solid	Raman[c] Solid	Raman[c] Solution	Calcd	PED		
1	3254 m	3261	3274 p	3253	$98F_1$		
2	2915 m	2919	2922	2918	$100F_2$		
3	2874 w	2882	2889 p	2874	$97F_3$		
4	1410 vw			1414	$97F_4$		
5	1263 s			1265	$71F_5$,	$28F_1$	
6	1173 s	1173 sh	1185 p	1175	$92F_6$		
7	712 s	706	705	715	$89F_7$		
8	533 m	525	524 p	539	$70F_8$,	$20F_9$	
9	461 w	457	451 p	470	$68F_9$,	$22F_8$	
10	188 w	184		184	$93F_{10}$		
16	3312 s	3320		3317	$100F_{16}$		
17	2915 m	2919	2922	2920	$99F_{17}$		
18	2915 m	2919	2922	2919	$99F_{18}$		
19	2874 w	2882	2889	2875	$98F_{19}$		
20	1615 w			1617	$100F_{20}$		
21	1470 vw	1436	1436	1445	$96F_{21}$		
22	1410 vw			1414	$96F_{22}$		
23		1163		1170	$92F_{23}$		
24	712 s	706	705	716	$68F_{24}$,	$14F_{27}$,	$10F_{26}$
25	743 s	737	734	750	$73F_{25}$.	$14F_{26}$	
26	743 s	737	734	743	$70F_{26}$,	$24F_{25}$	
27	608 s	605	597	619	$62F_{27}$,	$23F_{24}$	
28	214 m	215		213	$87F_{28}$		
29	171 m	167		168	$94F_{29}$		

a) Abbreviations: v, very; w, weak; m, medium; s, strong; sh, shoulder; p, polarized. b) Vibrational modes referring to the numbers are given in Table 5. c) Raman intensities are not given since photomultiplier sensitivity varies in a wide range within the spectral region.

Table 2. Observed and calculated frequencies (cm^{-1}) for $(CD_3)_3AlNH_3$[a]

No.[b]	Infrared Solid	Raman[c] Solid	Raman[c] Solution	Calcd	PED		
1	3252 m	3260	3276 p	3253	$98F_1$		
2	2179 m	2182	2184	2171	$99F_2$		
3	2089 w	2096	2100 p	2088	$94F_3$		
4	(1021)[d]		1033 p?	1021	$98F_4$		
5	1265 s	1269	1265	1265	$71F_5$,	$28F_1$	
6	914 w	916	921 p	910	$81F_6$,	$12F_8$	
7	586 s	594	580 p	588	$51F_7$,	$28F_9$	
8	482 w	474	469 p	475	$40F_8$,	$36F_7$,	$21F_9$
9		440	423 p	441	$46F_9$,	$39F_8$	
10	165 w	155		167	$91F_{10}$		
16	3312 s	3331		3317	$100F_{16}$		
17	2184 m	2182	2184	2173	$91F_{17}$		
18	2179 m	2182	2184	2171	$91F_{18}$		
19	2089 w	2096	2100	2086	$98F_{19}$		
20	1618 w			1617	$100F_{20}$		
21	(1038)[d]	1039	1042	1042	$97F_{21}$		
22	(1021)[d]			1021	$97F_{22}$		
23	923 s	924 sh	931 sh	915	$78F_{23}$,	$17F_{27}$	
24	716[e] s	703	696	710	$86F_{24}$		
25	586 s			556	$42F_{25}$,	$40F_{26}$,	$11F_{27}$
26	586 s			561	$44F_{26}$,	$51F_{25}$	
27	600 s	594		592	$65F_{27}$,	$14F_{24}$,	$11F_{23}$
28	187 m	185		188	$74F_{28}$,	$12F_{29}$	
29	154 m	143		156	$85F_{29}$,	$13F_{28}$	

a) For abbreviations, see Table 1. b, c) See the corresponding footnotes to Table 1. d) Frequencies in parentheses were not observed for this compound, but taken as the same values as those of the corresponding modes of $(CD_3)_3AlND_3$ for the normal coordinate calculations. e) This frequency is the average of 721 and 712 cm^{-1} observed as a doublet.

TABLE 3. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CH_3)_3AlND_3$$^{a)}$

No.$^{b)}$	Infrared Solid	Raman$^{c)}$ Solid	Raman$^{c)}$ Solution	Calcd	PED
1	2369 w	2373	2384 p	2370	$95F_1$
2	2910 s	2924	2920	2918	$100F_2$
3	2872 w	2883	2886 p	2874	$97F_3$
4	1410 vw		1407 p	1414	$97F_4$
5	974 s	987		971	$65F_5$, $30F_1$
6	1172 s	1177 sh	1179 p	1175	$94F_6$
7	710 s	716	711	713	$90F_7$
8	532 m	525	521 p	535	$81F_8$, $10F_9$
9	439 w	434	398 p	442	$75F_9$, $11F_8$
10	180 w	183	184	180	$91F_{10}$
16	2463 s	2484	2500	2459	$99F_{16}$
17	2910 s	2924	2920	2920	$99F_{17}$
18	2910 s	2924	2920	2918	$99F_{18}$
19	2872 w	2883	2886	2875	$98F_{19}$
20	1180 sh			1180	$99F_{20}$
21	1470 vw	1436	1436	1445	$96F_{21}$
22	1410 vw		1407	1414	$96F_{22}$
23		1165		1170	$92F_{23}$
24	501 m	497		495	$86F_{24}$
25	720 s	716	716	749	$80F_{25}$, $11F_{26}$
26	710 s	716	711	744	$76F_{26}$, $17F_{25}$
27	654 s	650	636	656	$72F_{27}$, $13F_{26}$
28	211 m	203		212	$89F_{28}$
29	160 m	165	156	160	$93F_{29}$

a) For abbreviations, see Table 1. b, c) See the corresponding footnotes to Table 1.

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) FOR $(CD_3)_3AlND_3$$^{a)}$

No.$^{b)}$	Infrared Solid	Raman$^{c)}$ Solid	Raman$^{c)}$ Solution	Calcd	PED
1	2373 w	2377	2385 p	2370	$95F_1$
2	2177 s	2187	2182	2171	$99F_2$
3	2090 w	2093	2097 p	2088	$94F_3$
4	1021 w			1021	$98F_4$
5	971 s	974		971	$65F_5$, $30F_1$
6	913 m	912	919 p	910	$81F_6$, $12F_8$
7	584 s	585	580 p	579	$59F_7$, $17F_9$
8	478 w	473	469 p	471	$60F_8$, $24F_7$
9	435 w	415	392	419	$59F_9$, $17F_8$, $11F_5$
10	162 w	150	165	163	$90F_{10}$
16	2468 s	2485	2500	2459	$99F_{16}$
17	2184 s	2187	2182	2173	$91F_{17}$
18	2177 s	2187	2182	2171	$91F_{18}$
19	2090 w	2093	2097	2086	$95F_{19}$
20	1180 vw			1180	$99F_{20}$
21	1038 w	1037	1035	1042	$97F_{21}$
22	1021 w			1021	$97F_{22}$
23	921 s	924 sh	928 sh	914	$77F_{23}$, $17F_{27}$
24		490 sh		490	$80F_{24}$, $13F_{27}$
25	584 s			559	$83F_{25}$
26	584 s			562	$83F_{26}$
27	628 s	629	637	622	$63F_{27}$, $12F_{24}$, $11F_{23}$
28	184 m	180		187	$80F_{28}$
29	146 m	150	141	149	$89F_{29}$

a) For abbreviations, see Table 1. b, c) See the corresponding footnotes to Table 1.

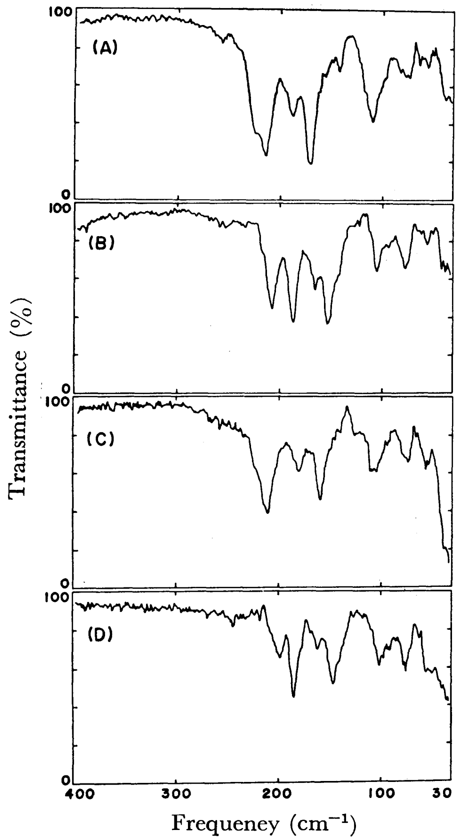

Fig. 2. Far infrared spectra of (A) $(CH_3)_3AlNH_3$, (B) $(CD_3)_3AlNH_3$, (C) $(CH_3)_3AlND_3$, and (D) $(CD_3)_3$-$AlND_3$ recorded at −196°.

group.

The NH_3 rock is observed at 712 cm^{-1} coinciding with the CH_3 (A_1) rocking frequency for $(CH_3)_3AlNH_3$, and at 721 and 712 cm^{-1} as a doublet for $(CD_3)_3AlNH_3$. The mode shifts to 501 cm^{-1} for $(CH_3)_3AlND_3$. For $(CD_3)_3AlND_3$, no absorption is found around 500 cm^{-1}, but a shoulder is observed at 490 cm^{-1} in the Raman spectrum and assigned to the ND_3 rock.

Skeletal Modes. The symmetric AlC_3 stretches are observed at almost definite frequency of 530 cm^{-1} for the $(CH_3)_3Al$ and of 480 cm^{-1} for the $(CD_3)_3Al$ adducts. The mode gives the strongest polarized Raman line. The degenerate AlC_3 stretch, coupling with deformation of the methyl and ammonia groups, is observed in the 650—600 cm^{-1} region.

The AlC_3 deformation is observed in the 210—150 cm^{-1} region (Tables 1—4).

The Al–N stretch is observed in the 460—435 cm^{-1} region in the infrared spectrum. The absorption is weak, and not observed for $(CD_3)_3AlNH_3$. The corresponding Raman band is weak, but polarized. In a solution Raman spectrum, this mode is observed to shift toward the lower frequency than that in the solid state.

Normal Coordinate Calculations

The normal coordinate analysis was undertaken to confirm the assignments. The calculation was made by Wilson's *GF* matrix method on an ACOS 77/700 computer at the Computer Center, Tohoku University,

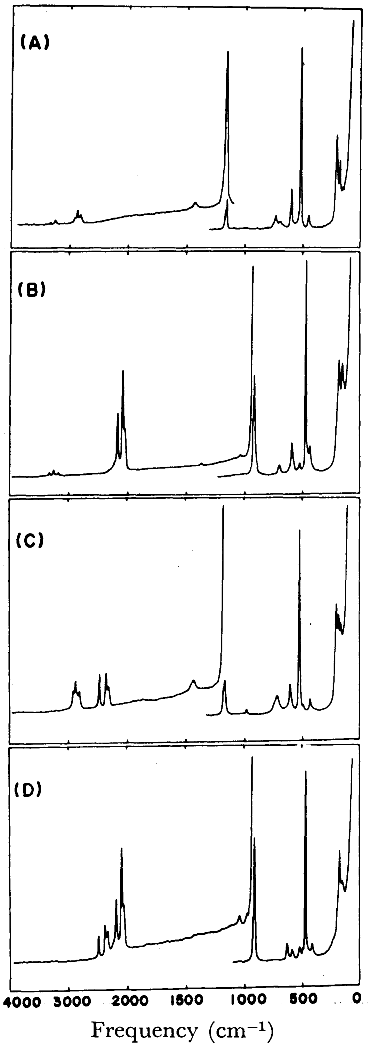

Fig. 3. Raman spectra of (A) $(CH_3)_3AlNH_3$, (B) $(CD_3)_3$-$AlNH_3$, (C) $(CH_3)_3AlND_3$, and (D) $(CD_3)_3AlND_3$ recorded in the solid state at ambient temperature.

by means of the usual iterative least-squares procedure.

The *G* matrix was calculated using structural parameters of Cl_3AlNH_3[10] and $(CH_3)_3AlN(CH_3)_3$[11] determined by electron-diffraction studies; r(N–H) = 1.03 Å (assumed), r(C–H) = 1.09 Å, r(Al–C) = 1.987 Å, r(Al–N) = 2.099 Å (taken from $(CH_3)_3AlN(CH_3)_3$), ∠(H–N–H) = 112.79°, ∠(Al–C–H) = 111.8°, and ∠(C–Al–N) = 102.3°. Symmetry coordinates similar to those for trimethylarsine-borane[12] were used.

Infrared frequencies were used for the calculations. The Raman frequencies observed in the solid state were used for vibrations which frequencies were not accurate from the infrared spectra but accurate enough from the Raman effect. The torsional mode was neglected in the E class. The frequencies were weighted by $(1/\lambda)$ in the least-squares routine, but the CH_3 degenerate deformation frequencies were weighted by 0.1 because of inaccuracy. The least-squares refinement was carried out in terms of symmetry force constants, fitted to the observed frequencies for the four isotopic species simultaneously. The calculated frequencies are given for the four isotopic species in Tables 1—4, together with the potential energy distributions, the average

Table 5. Symmetry force constants and their uncertainties for trimethylaluminium-ammonia[a)]

			σ				σ
ν(NH_3)	F_1	5.593	0.087	ν(NH_3)	E_{16}	5.919	0.027
ν(CH_3)	F_2	4.543	0.009	ν(CH_3)	F_{17}	4.551	0.023
ν(CH_3)	F_3	4.642	0.042	ν(CH_3)	F_{18}	4.542	0.023
δ(CH_3)	F_4	0.548	0.003	ν(CH_3)	F_{19}	4.667	0.092
δ(NH_3)	F_5	0.689	0.033	δ(NH_3)	F_{20}	0.595	0.013
δ(CH_3)	F_6	0.400	0.009	δ(CH_3)	F_{21}	0.571	0.009
ρ(CH_3)	F_7	0.332	0.004	δ(CH_3)	F_{22}	0.547	0.009
ν(AlC_3)	F_8	2.312	0.063	δ(CH_3)	F_{23}	0.391	0.018
ν(AlN)	F_9	1.544	0.059	ρ(NH_3)	F_{24}	0.300	0.030
δ(AlC_3)	F_{10}	0.508	0.017	ρ(CH_3)	F_{25}	0.400	0.009
				ρ(CH_3)	F_{26}	0.381	0.009
	$F_{1,5}$	−0.992	0.069	ν(AlC_3)	F_{27}	2.087	0.098
	$F_{3,6}$	−0.214	0.065	δ(AlC_3)	F_{28}	0.482	0.036
	$F_{6,8}$	−0.103	0.028	ρ(AlC_3)	F_{29}	0.409	0.037
	$F_{5,9}$	0.073	0.033				
	$F_{8,9}$	0.082	0.040		$F_{19,23}$	−0.175	0.157
					$F_{20,24}$	−0.089	0.115
					$F_{23,27}$	−0.090	0.045
					$F_{24,27}$	0.032	0.017
					$F_{26,27}$	0.198	0.076

a) Stretching force constants in mdyn/Å, bending constants in mdyn Å/(radian)^2, stretching-bending interactions in mdyn/radian. ν, stretching; δ, deformation; ρ, rocking; σ, dispersion.

errors being 0.51 and 0.97% for the A_1 and E vibrations, respectively. The sum of the weighted squares of errors, $\Sigma(\lambda_{obsd}-\lambda_{calcd})^2/\lambda_{obsd}$, was 1.83×10^{-3} for the A_1 species vibrations and 1.45×10^{-2} for the E species. The symmetry force constants and their uncertainties from the last cycle of the least-squares refinement are given in Table 5.

Discussion

In the far infrared spectra, another absorption in the skeletal deformation region was observed at around 220 cm^{-1} as a shoulder for the $(CH_3)_3Al$ adduct and at about 200 cm^{-1} for the $(CD_3)_3Al$, which remained unassigned. This may be due to the torsional mode of the methyl groups active in both the infrared and the Raman spectrum. They seem to be rather intense as being due to torsions, the deuteration shift (20 cm^{-1}) appearing to be too small.[13)] An infrared strong absorption at 604 cm^{-1} of $(CH_3)_3AlND_3$ also remained unassigned. Attempts to assign the vibrational mode was unsuccessful.

The symmetric AlC_3 stretch is mixed with the Al–N stretch, also with the CD_3 rock for the $(CD_3)_3Al$ adduct. The frequencies are in almost fixed region at 530 cm^{-1} for the $(CH_3)_3Al$ adducts and at 480 cm^{-1} for the $(CD_3)_3Al$, not being influenced on deuteration of the ammonia group, whereas the degenerate AlC_3 stretch is mixed with the NH_3 or ND_3 rock and the frequencies are higher for the ND_3 adducts than those of the NH_3.

Studies on boron adducts have shown the Raman technique to be more sensitive to the donor-acceptor bond stretching mode than the infrared technique.[14–17)] The Al–N stretch of the $(CH_3)_3AlNH_3$ molecule is weak in intensity in the infrared spectrum and also unexpectedly weak in the Raman effect.

Agreement between the observed and calculated frequencies is satisfactory. The vibrational assignments are supported by the product rule ratios given in Table 6, where the theoretical ratios were calculated from the determinant of the *G* matrices.

The Al–N force constant is compared with that of

Table 6. Comparison of product rule ratios for the various isotopic combinations of the $(CH_3)_3AlNH_3$ molecule[a)]

	A_1		E	
	Calcd	Theoret.	Calcd	Theoret.
$(CH_3)_3AlNH_3/(CD_3)_3AlND_3$	9.79	9.68	34.4	32.6
$(CD_3)_3AlNH_3/(CD_3)_3AlND_3$	1.91	1.90	2.78	2.66
$(CH_3)_3AlND_3/(CD_3)_3AlND_3$	4.96	4.93	12.1	11.9
$(CH_3)_3AlNH_3/(CH_3)_3AlND_3$	1.97	1.96	2.85	2.74
$(CD_3)_3AlNH_3/(CH_3)_3AlND_3$	0.385	0.386	0.230	0.223
$(CH_3)_3AlNH_3/(CD_3)_3AlNH_3$	5.12	5.07	12.4	12.2

a) The theoretical values were calculated from the determinants of the *G* matrix, as $|G|/|G'|$.

TABLE 7. COMPARISON OF BOND DISTANCES, STRETCHING FORCE CONSTANTS AND STRETCHING FREQUENCIES OF Al–N BOND, AND HEATS OF FORMATION

	r(Al–N) Å	f(Al–N) mdyn/Å	ν(Al–N) cm^{-1}	$-\Delta H$ kJ/mol
$Cl_3AlN(CH_3)_3$	1.96[18] 1.945[19]	2.251[4]	565[4]	198.7[11]
Cl_3AlNH_3	1.996[10]	1.912[4] 1.875[21]	579[4]	
$H_3AlN(CH_3)_3$	2.063[20]	2.321[4]	525[4] 533[22]	
$(CH_3)_3AlN(CH_3)_3$	2.099[11]			125.3[23] 128.4[11]
$(CH_3)_3AlNH_3$		1.544[a]	461[a]	115.2[23]

a) This work.

other addition compounds containing an Al–N bond in Table 7, where their Al–N bond distances, Al–N stretching frequencies and heats of formation are also given. We can not find any trend from the frequencies of the Al–N stretching mode, probably because of its mixing with other vibrational modes. However, we find correlations between the bond distances, the Al–N force constants (except that of $H_3AlN(CH_3)_3$) and the heats of formation. Considering that ammonia is a weaker base than trimethylamine and the heat of formation of $(CH_3)_3AlNH_3$ is less than that of $(CH_3)_3AlN(CH_3)_3$, the Al–N bond distance of $(CH_3)_3AlNH_3$ would be greater than that of $(CH_3)_3AlN(CH_3)_3$. The force constant 2.321 mdyn/Å for $H_3AlN(CH_3)_3$ seems quite large as compared with the Al–N bond distances. Though we have only a limited number of data and detailed vibrational analysis would be necessary for other compounds, it appears that the Al–N force constant of 1.544 mdyn/Å is reasonable for trimethylaluminium-ammonia.

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