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G. N. Papatheodorou, L. A. Curtiss, and V. A. Maroni

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Raman spectra, *ab initio* molecular orbital calculations, vibrational analysis, and thermodynamic functions for NH_3 :AIX₃ (X = F, CI, Br)^{a)}

G. N. Papatheodorou, L. A. Curtiss, and V. A. Maroni

Argonne National Laboratory, Argonne, Illinois 60439 (Received 26 May 1982; accepted 7 December 1982)

Raman spectra of gaseous NH₃:AlCl₃ and NH₃:AlBr₃ were recorded at 400 °C. The observed Raman frequencies in combination with reported infrared frequencies for NH₃:AlCl₃ and *ab initio* molecular orbital calculations on NH₃:AlCl₃ and NH₃:AlF₃ were used to derive force constants for all three NH₃:AlX₃ complexes (X = F, Cl, Br) based on an adjusted valence force field (AVFF) concept. The resulting force constant calculations produced complete sets of A_1 and E mode frequencies for each complex. Statistical mechanical analyses were then performed using the A_1 and E mode frequencies together with estimated values for the torsional mode of each complex and published enthalpy data. From these analyses, the relative thermodynamic stability of each complex was determined. At 700 and 1000 K, NH₃:AlCl₃ was found to be more stable than NH₃:AlF₃. It was further predicted that the reaction of gaseous NH₃ with solid AlF₃ to form NH₃:AlF₃ is not favored in this temperature range, which provides an explanation for the lack of success in prior efforts to produce NH₃:AlF₃.

I. INTRODUCTION

It has been well established that aluminum halides react with ammonia to form donor : acceptor type solid or liquid compounds with the stoichiometry nNH_3 : AlX_3 (X = Cl, Br, I; n = 1-6).¹ Evolution of NH_3 occurs when these compounds are heated to 100-200 °C under vacuum, yielding stable compounds with the stoichiometry NH_3 : AlX_3 . These amine-aluminum halide "complexes" and the corresponding ammonium-tetrahaloaluminate salts NH_4AlX_4 have been the subject of a number of thorough investigations.²⁻¹⁵ Volatilization of the NH_4AlX_4 salts occur with dissociation^{2,3}

$$NH_4AlX_4(l) \rightarrow NH_3: AlX_3(g) + HX(g)$$
(1)

and heating of the amine halide vapor leads to the vapor equilibrium

$$NH_3: AlX_3(g) \rightarrow NH_3(g) + AlX_3(g) . \tag{2}$$

The dissociation according to the reaction in Eq. (2) at $450 \,^{\circ}\text{C}$ is minimal for the chloride⁴ (K_{eq} at $450 \,^{\circ}\text{C} \simeq 10^{-4}$ atm), is appreciable for the bromide⁵ (K_{eq} at $450 \,^{\circ}\text{C} \simeq 1$ atm), and is complete for the iodide.⁵ Finally, heating the amine chloride or bromide above 800 $^{\circ}\text{C}$ results in decomposition and deposition of refractory aluminum nitride

$$NH_3: AlX_3(g) \rightarrow AlN(s) + 3HX(g) . \tag{3}$$

Similar decomposition of the iodide has been reported to occur at even lower temperatures (i. e., ≤ 200 °C).⁵ Thus far, no evidence for the existence of the NH₃: AlF₃ complex in either the condensed or gaseous state has been reported.

Hargittai *et al.*, 6-8 have established the molecular structure of the amine chloride and bromide vapor phase

complexes by careful electron diffraction studies. A staggered $C_{3\nu}$ (ethane-like) structure has been proposed, where NH₃ and AlX₃ are pyramidally shaped and bound to each other by an Al-N bond. Raman and IR studies have been reported for liquid and solid NH₃: AlCl₃. ⁹⁻¹² Assignments of the vibrational frequencies of the liquid have been made, assuming a molecular liquid consisting of NH₃: AlCl₃ entities. ¹¹ Cyvin *et al.* ¹³ combined the liquid phase vibrational spectra and the vapor electron diffraction data to provide a normal coordinate analysis and force field calculation for gaseous NH₃: AlCl₃. Recently, however, it has been shown^{3,14} that the Raman spectrum of NH₃: AlCl₃ in the vapor state is distinctly different from that of the liquid or glassy state.

The present examination concerns the spectroscopic, structural, thermochemical, and bonding properties of the gaseous NH_3 : AlX₃ (X = F, Cl, Br) complexes. (Preliminary reports of some of these studies are presented elsewhere.^{3,15}) Vapor phase Raman spectra of the amine chloride and bromide have been measured and assignments of all observed vibrational frequencies made. Ab initio molecular orbital (MO) calculations have been carried out for the amine fluoride and chloride to provide a better understanding of the bonding and molecular geometries of these species. The experimental (Raman) and theoretical (MO) results, together with some unpublished infrared data¹⁶ for gaseous NH₃: AlCl₃, have been used to carry out a complete vibrational analysis and force field calculation for all three halide complexes. The question of the existence and thermodynamic stability of the NH₃: AlF₃ complex is examined and the thermodynamic properties of all three vapor complexes are calculated and compared.

Finally, it is worth noting that the amine halide complexes, especially NH_3 : AlCl₃, are important for a variety of potential applications related to energy conservation and to aluminum production, ^{17,18} as well as to molten salt processing of nuclear fuels. ¹⁹

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FIG. 1. Raman spectra of NH₃: AlCl₃(g) at ~400°C; $\lambda_0 = 514.4$ nm, power ~4.5 W, scan speed 5 cm⁻¹/min, spectral slit width ~5.5 cm⁻¹, time constant $\tau = 3$ s, except for the 50–140 cm⁻¹ region where $\tau = 2$ s. The cell had been previously used for spectra at higher temperatures; the NH₃ gas present is a result of reaction of the amine with the SiO₂ container.

II. RAMAN SPECTRA AND ASSIGNMENTS

Raman spectra of the amine chloride and bromide vapor complexes at elevated temperatures were obtained by methods described in more detail elsewhere.⁸ Evacuated and sealed fused silica cells containing the salts were placed in a resistance heated furnace and the vapor spectra were excited with an Ar^* CW laser (~15 W all lines). The scattered radiation was dispersed with a double monochromator and detected with a photomultiplier tube using photon counting techniques.

The NH_3 : AlCl₃(g) spectra were obtained for samples prepared by the following three methods:

(1) Solid NH_3 : AlCl₃ was synthesized by reacting equimolar amounts of AlCl₃ and NH_3 as in Ref. 1. Weighed amounts of the solid were then sealed in Raman cells, giving a calculated pressure of ~1 atm at ~500 °C. A typical spectrum obtained by this method is shown in Fig. 1. Spectra obtained from cells kept below $500 \,^{\circ}\text{C}$ did not show the presence of small amounts of $\text{NH}_3(\text{g})$. However, repeated use of a cell and/or extensive heating over $500 \,^{\circ}\text{C}$ resulted in the formation of $\text{NH}_3(\text{g})$. This was presumably due to the loss of $\text{AlCl}_3(\text{g})$ caused by its reaction with the silica cell to form Al_2O_3 . The spec-trum displayed in Fig. 1 was measured in a cell previously heated to $700 \,^{\circ}\text{C}$. It also contains the NH_3 symmetrical stretching mode, as well as a series of weak, low-frequency rotational bands due to NH_3 (see the 200- $300 \, \text{cm}^{-1}$ region).

(2) Approximately equimolar amounts of $AlCl_3(s)$ and $NH_3(g)$ (~0.5 atm) were introduced directly into the Raman cell. The cell was then cooled to liquid nitrogen temperature (to solidify the NH_3) and sealed under vacuum. Spectra measured with these cells were the same as those in Fig. 1.

(3) Solid NH_4AlCl_4 was synthesized by reacting equimolar amounts of solid NH_4Cl and $AlCl_3$, and Raman spectra of the vapor over liquid NH_4AlCl_4 [see the reaction in Eq. (1)] were recorded in the temperature range 400-700 °C. The spectra consisted of a superposition of the vibrational bands of NH_3 : $AlCl_3$ and the pure rotational and vibrational-rotational bands of HCl.

All of the above methods resulted in the observation of bands that can readily be assigned to NH_3 : $AlCl_3$. The measured frequencies and their uncertainties are listed in Table I.

Due to the dissociative reaction in Eq. (2) given above, the NH_3 : $AlBr_3$ complex is rather difficult to prepare as a solid and thus spectra of its vapor were obtained in a manner similar to methods 2 and 3 described above for the chloride complex. Figure 2 shows a spectrum obtained for the vapor over $NH_4AlBr_4(l)$. A superposition of spectra resulting from all species participating in the reactions in Eqs. (1) and (2) is present. Temperature dependence studies and comparisons with the high-temperature spectra of gaseous HBr and NH_3 were used to identify the vibrational frequencies due to NH_3 : $AlBr_3$. These frequencies are also listed in Table I.

The NH_3 : AlX₃ complex with either a staggered or an eclipsed configuration possesses $C_{3\nu}$ point group sym-



FIG. 2. Raman spectra of vapors over NH₄AlBr₄ liquid at ~ 400°C, λ_0 = 514.5 nm, power ~ 2 W, scan speed 20 cm⁻¹/min, spectral slit width ~ 4 cm⁻¹ (0-600 cm⁻¹ region) and 7.5 cm⁻¹ (2100-3500 cm⁻¹ region), time constant $\tau = 0.4$ s (0-600 cm⁻¹) and τ = 0.8 s (2100-3500 cm⁻¹). The spectra presented are a superposition of NH₃: AlBr₃(g), HBr(g), and NH₃(g) vibrational and rotational spectra.

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NH ₃ : AlCl ₃	(400°C)	AlCl ₃ (400°C) ^b	NH ₃ (4	00°C) ^b	AlBr ₃ (400°C) ^b		NH3:AlBr3 (400°C)	
Frequency cm ⁻¹	Assignment	Frequency cm ⁻¹	Assignment	Frequency cm ⁻¹	Assignment	Frequency cm ⁻¹	Assignment	Frequency cm ⁻¹	Assignment
						04 a	н (Е /)	85 ±1 s	E
$125 \pm 1 s$) ^c $133 \pm 1 s$	Ε	135 ± 2 s	$\nu_4(E')$			94 8	V4 (E)		
100118/						(155)	$\nu_2(A_2'')$ inactive		
$\sim 175 \text{ sh}$	(?)	(183)	$\nu_{\rm s}(A^{\prime\prime})$					$149 \pm 2 s, p$	A ₁
		(100)	inactive						
200±1 m,p	A ₁					230 s,p	$\nu_i(A_i)$	255 ± 1 s,p	A_1
$311 \pm 3 \text{ vw}$	combination		. (•
377.5 ± 1 s,p 400 ± 1 m,p	A ₁ overtone	375 s,p	$\nu_{i}(A_{i})$					$440 \pm 5 w$	E
~480 w,p	A _i					510 w	$\nu_{\rm e}(E')$		
525 ± 5 m,br	E					010 w	-34-7	(1595)	E
(1597) †	E	610 W	ν ₃ (Ε ')	~920 vw,p	$\nu_2(A_1)$			Î	
3195 ±2 w, p	overtone			1627 vw	$\nu_4(E)$			3189 w,p	overtone
3300 ± 2 s, p 3387 ± 5 w, br	A ₁ E			3377 s,p 3444 w	$ \nu_1(A_1) \\ \nu_3(E) $			3294±2 s,p 3390±5 w,br	<i>A</i> ₁ <i>E</i>

TABLE I. Experimental Raman active vibrational frequencies and assignments for gaseous NH_2 : AIX ₂ (X = CI, Br). AICI ₂ , AIBr ₂ ,
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^aNotation: s=strong, m=medium, w=weak, p=polarized, v=very, sh=shoulder, br=broad.

^bWork in progress. ^cVibration-rotation doublet.

metry. The 18 normal modes of vibration are distributed TABLE II. STO-3G optimized geometries² for NH₃, AlF₃, and among the symmetry species as follows¹³:

$$\Gamma = 5A_1(\mathbf{R}, \mathbf{IR}) + A_2(\mathbf{IA}) + 6E(\mathbf{R}, \mathbf{IR})$$
(4)

with Raman (R), infrared (IR), and inactive (IA) modes indicated in parenthesis. Assignments of the bands observed for the two molecules are given in Table I. In the same table, the Raman frequencies and assignments for the AlX₃ (X = Cl, Br) and NH₃ gaseous molecules measured at elevated temperature are also given.

Noteworthy features of the results in Figs. 1 and 2 and in Table I are that the high frequency region (above 3000 cm⁻¹) of the spectra for NH₃: AlCl₃ and NH₃: AlBr₃ contain bands whose positions are close to those of the corresponding N-H symmetric and antisymmetric stretching modes of gaseous NH₃. Further, the very weak intensity of the H-N-H bending modes (920 and 1627 cm⁻¹) in the Raman spectrum of pure NH₃ may account for why these corresponding bands are not observed for the NH₃: AlX₃ complexes.

The features of the spectra of NH3: AlCl3 and NH₃: AlBr₃ (particulary below 600 cm⁻¹) closely parallel those of other $MX_3: Y$ type molecules,²⁰ where MX_3 is the aluminum halide in a pyramidal configuration. The vibrational-rotational splitting of the lowest frequency band observed for the MX₃: Y molecules is also resolved in the lowest frequency mode of NH₃: AlCl₃. The sharp polarized band at 400 cm⁻¹ for NH₃: AlCl₃ has no counterpart in the NH₃: AlBr₃ spectrum. Its intensity was found to change with temperature relative to that of the strong 377.5 cm⁻¹ band; hence, it was attributed to the first overtone of the 200 cm^{-1} band.

The polarization of the weak NH_3 : AlCl₃ band at ~480 cm⁻¹ was confirmed by measurement of the linear depolarization ratio from 400-600 cm⁻¹ and this band was attributed to the Al-N stretching vibration. The frequency at ~480 cm^{-1} is lower than the 581 cm^{-1} value found for solid NH_3 : AlCl₃, ¹² but the Al-N distance in the solid¹² is shorter than the gas phase value by 0.07 Å.

For both NH_3 : AlCl₃ and NH_3 : AlBr₃ no bands were measured in the 600-3100 cm⁻¹ region. The band observed near 3190 cm⁻¹ for both complexes is attributed to the first overtone of the doubly degenerate H-N-H bending mode (possibly enhanced in intensity by Fermi resonance with the totally symmetric N-H stretching mode of the complex). This band is the counterpart of the very weak $\nu_4(E)$ bending mode of $NH_3(g)$. Systematic studies of a series of amine complexes have shown^{21(a)} that the nontotally symmetric NH₃ bending mode is affected very little by changes in M and, for most complexes, has a value in the range 1620 ± 30 cm⁻¹. The symmetric bending mode, on the other hand, normally increases to values near 1200 cm⁻¹ upon complexation of NH₃.

The assignment of the fundamental frequencies given in Table I is supported by the following: (a) intensity and polarization measurements show that the assigned A_1 bands are the strongest and are measurably polarized, while the depolarization ratio is close to $\frac{3}{4}$ for all normal modes assigned to the symmetry species E; (b) the

AlCl₃. (Experimental values are given in parentheses).

Molecule	r, Å	θ, deg	Energy, a.u. ^e
NH3b AlF3c AlCl3d	1.03(1.01)	104.2(106.7)	- 55.45542
	1.60(1.63 \pm 0.01)	120.0(120)	- 533.24983
	2.05(2.06 \pm 0.01)	120.0(118±1.5)	- 1603.02719

 ${}^{a}C_{3v}$ minimum symmetry assumed.

- ^bTheory: W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, J. Am. Chem. Soc. 93, 6377 (1971). Experiment: K. Kuchitsu, J. P. Guillory, and L. S. Bartell, J. Chem. Phys. 49, 2488 (1968).
- ^cTheory: Ref. 15. Experiment: P. A. Akishin, N. G. Rambidi, and E. A. Zasorin, Kristallografiya 4, 186 (1959) [Sov. Phys. Crystallogr. 4, 167 (1959)].
- ^dTheory: Ref. 15. Experiment: E. Z. Zasorin and N. G. Rambidi, Zh. Strukt. Khim. 8, 391 (1967).

°1 a.u. =627.5 kcal mol⁻¹.

frequencies and band intensities of NH3: AlCl3 and NH3: AlBr3 are well correlated with the frequencies and band intensities of $AlX_3(g)$ (X = Cl, Br) and $NH_3(g)$; and (c) the results of the normal coordinate analyses (discussed below) are consistent with the proposed assignments.

Following the preparation of an earlier version of this paper, the authors were made aware of a recent infrared spectroscopic study of gaseous NH₃: AlCl₃.¹⁶ Although unpublished, the results of that study have nonetheless been combined with the Raman data in Table I in order to provide the most complete analysis possible for NH₃: AlCl₃. The infrared spectrum was found to contain bands which corresponded reasonably well with the Raman bands at 125/133 cm⁻¹, 200 cm⁻¹, 377.5 cm⁻¹, and 480 cm^{-1} . Additional strong bands were observed in the infrared spectrum at 1261 and 697 cm⁻¹. These latter two bands were incorporated into the vibrational analysis reported herein as the missing H-N-H symmetric bend (A_1) and as one of the two missing E modes of NH_3 : AlCl₃, respectively.

III. AB INITIO MOLECULAR ORBITAL CALCULATIONS

Ab initio molecular orbital calculations were carried out on NH₃: AlF₃ and NH₃: AlCl₃. Structures, energies and force constants were calculated for use in the vibrational analyses in Sec. IV and in the calculation of the thermodynamic functions in Sec. V. Standard LCAO-SCF methods were utilized in this study. The basis set employed was the minimal STO-3G basis, 22 which has been used in a number of prior studies of metal halide complexes. 15,23,24 The optimized STO-3G geometries for AlF₃, AlCl₃, and NH₃ are given in Table II.

The ethane-like structure with C_{3v} symmetry considered for NH_3 : AlF₃ and NH_3 : AlCl₃ is illustrated in Fig. 3(a). The geometry and rotational conformation of each complex were determined. In the geometry optimization procedure used here, all of the parameters were optimized with respect to the total energy, while maintaining C_{3v} symmetry. The bond lengths and bond angles were



FIG. 3. NH_3 : AlX₃ structure and configurational representations of the internal coordinates used in the vibrational analysis.

optimized until they changed less than 0.01 Å and 1°, respectively. Staggered ($\phi = 180^{\circ}$) and eclipsed ($\phi = 0^{\circ}$) forms of the complexes were investigated. In the case of NH₃: AlF₃, the eclipsed structure was only 0.33 kcal mol⁻¹ more stable than the staggered, while in the case of NH₃: AlCl₃ the staggered structure was only 0.13 kcal mol⁻¹ more stable than the eclipsed. The theoretical cal-

culations are not accurate enough to reliably predict which of the conformations is more stable; however, they do indicate that there is little resistance to rotation about the Al-N axis in both complexes.

The completely optimized geometries of the lowest energy structures, i. e., eclipsed NH_3 : AIF_3 and staggered NH_3 : $AlCl_3$, are listed in Table III. The possibility that the complexes do not have $C_{3\nu}$ symmetry was investigated by relaxing the NH_3 : AIF_3 symmetry to $C_{s\nu}$ i.e., by reducing the symmetry operations to a single plane of symmetry passing through the Al-Naxis, one of the hydrogens, and one of the fluorines. All distortions from $C_{3\nu}$ symmetry led to a higher energy, indicating that NH_3 : AIF_3 has a $C_{3\nu}$ equilibrium structure. This conclusion should also hold for NH_3 : $AlCl_3$.

The STO-3G optimized geometries for NH₃: AlCl₃ are in good agreement with the electron diffraction study of Hargittai *et al.*⁸ (see Table III). The experimental and theoretical changes in the bond lengths and bond angles of the monomers upon complex formation are in the same direction, the Cl-Al-Cl angle becomes smaller, the H-N-H angle opens up, and the Al-Cl bond length increases.

The complexation energies of the STO-3G optimized structures of NH_3 : AlF_3 and NH_3 : $AlCl_3$ are -41.3 kcal mol⁻¹ and -63.0 kcal mol⁻¹, respectively. Correcting for differences in vibrational, rotational, and translational energies between the monomers and the complexes gives theoretical enthaplies of association of -36.8 kcal mol⁻¹ and -57.9 kcal mol⁻¹ for NH_3 : AlF_3 and NH_3 : $AlCl_3$, respectively. It should be noted, however, that the STO-3G basis set tends to overestimate the interaction energies and that a larger basis set would be required to obtain more reliable energies.²³

Theoretical total force constants for the bond stretches in the NH_3 : AlF_3 and NH_3 : $AlCl_3$ complexes were calculated for use in the vibrational analysis presented in the next section. The total force constants were obtained by quadratic fitting to points near the minima of the STO-

TABLE III. Optimized geometries and experimental structures for NH₃: AlX₃ complexes.

Geometrical parameter ^a	NH ₃ :	AlF ₃	NH	3 : AlCl ₃	NH ₃ :AlBr ₃	
	Calc. ^b	Expt.	Calc, c	Expt.d,e	Calc.	Expt.d,e
r(A1-N), Å	1.99	•••	1.94	1.998±0.019	•••	1,999±0,019
r(A1-X), Å	1.62	•••	2.08	2.102 ± 0.005	• • •	$2,266 \pm 0,005$
r(N-H), Å	1.03	• • •	1.03	(1,030)	•••	1.063 ± 0.033
(XA1X, deg.	117.0	•••	116.4	116.9 ± 0.4	• • •	115.7 ± 3
(HNH, deg.	106.6	•••	106.3	112.8 ± 3.5	•••	114.5 ± 4.0
φ, deg	0.0	•••	180.0	(180)	• • •	(180)
I _x I _y I _x ⁱ	0.3117	•••	•••	4,473	• • •	56.72

^aSee Fig. 3(a) for illustration of structure ($\phi = 180^\circ$ corresponds to the staggered configuration, $\phi = 0^\circ$ corresponds to the eclipsed configuration).

^bTotal energy E = -588.77159 a.u.

 $^{\circ}$ Total energy E = -1658.58296 a.u.

dRefs. 6-8.

"Values in parentheses have been assumed.

⁴Products of moments of inertia used in calculation of thermodynamic functions. Units of 10¹¹⁰ g³ cm⁶.

		Observ	ed and calcu	lated freque	encies, cm		1	Potential en	arav	
Symmetry	NH ₃ : AlF ₃		NH ₃ :AlCl ₃		NH ₃ : AlBr ₃		Principal internal	distribution ^e		
species	MO ^a	AVFF ^a	Obs. ^a	AVFF ^a	Obs.	AVFF	coordinate(s)	F	C1	Br
1	3881	3324	3300	3300	3294	3295	N-H	(100)	(100)	(100)
	1564	1487	(1261) ^b	1261		1160	H–N–H/H–N–Al	(63/24)	(54/35)	(49/40)
$A_1 \langle$	544	521	480	480		467	Al-N	(75)	(88)	(91)
1	783	667	378	378	255	254	Al-X	(89)	(94)	(84)
	317	271	200	200	149	149	N-Al-X/X-Al-X	(71/12)	(81/12)	(69/15)
A_2	149	•••	• • •	•••	•••	•••	Torsion	(100)	(100)	(100)
1	4120	3374	3387	3387	3390	3389	N-H	(100)	(100)	(100)
	1986	1532	1597	1597	1595	1595	H-N-H	(100)	(100)	(100)
r (736	670	(697) ^b	697	•••	685	H-N-Al	(94)	(94)	(97)
E	1107	895	525	525	440	440	Al-X	(91)	(85)	(78)
	184	285		229	•••	188	X-Al-X/N-Al-X	(32/62)	(•••/87)	(•••/85)
	278	242	129	129	85	85	X-Al-X/N-Al-X	(65/34)	(95/•••)	(97/•••)

TABLE IV. Calculated and observed frequencies, assignments, and potential energy distributions for the $NH_3:AlX_3$ complexes (X = F, Cl, Br).

 $^{a}MO = Molecular orbital calculation: AVFF = calculated using AVFF; Obs = observed frequencies.$

^bFrom Ref. 16.

°Numbers in parentheses represent % contribution of principal internal coordinate; contributions of $\langle 10\%$ are neglected.

3G potential energy surfaces. The N-H and Al-X total symmetric stretching force constants F_s are 8.6 and 6.4 mdyn/Å, respectively, for NH₃: AlF₃ and 8.7 and 4.0 mdyn/Å, respectively, for NH₃: AlCl₃. The N-H and Al-X total antisymmetric stretching force constants F_a are 9.3 and 6.7 mdyn/Å, respectively, for NH₃: AlF₃ and 9.3 and 3.8 mdyn/Å, respectively, for NH₃: AlF₃. The Al-N stretching force constant is 2.0 mdyn/Å in NH₃: AlF₃ and 2.6 mdyn/Å in NH₃: AlCl₃. At this level of calculation, stretching force constants are generally found to be 20%-50% too large, ²⁵ but observed trends in related molecules should be preserved in the calculations.

The corresponding generalized valence force (GVFF) constants for the NH₃ and AlX₃ groups are obtained from the total symmetric and total antisymmetric, force constants by the relationship $K(\text{GVFF}) = (F_s + 2F_a)/3$. This relationship results from inspection of the GVFF contributions to the symmetrized *F*-matrix elements^{21(b)} for NH₃ and AlCl₃ and the assumption that the MO calculated values of F_s and F_a are equivalent to the corresponding diagonal elements of the symmetrized *F* matrices.

In addition to the calculation of the bond stretch and bond-bond interaction force constants described above, a gradient technique²⁶ has been used to obtain the complete set of STO-3G quadratic force constants for NH₃: AlF₃. The harmonic frequencies calculated from these force constants are given in Table IV for comparison with the frequencies derived for NH₃: AlF₃ from the vibrational analysis described in the next section. The MO frequencies are, as expected, too large by 10%-25%, but they are consistent with the predicted values. The MO results for NH₃: AlF₃ provide an estimate for the A_2 torsion frequency which is not observed for NH₃: AlCl₃ and NH₃: AlBr₃ and is not given by the vibrational analysis.

The Mulliken and atomic populations²⁷ of the NH_3 : AlF₃

and NH_3 : AlCl₃ complexes were calculated from the STO-3G wave functions. By adding up the atomic populations, the net charges on the NH_3 and AlX_3 groups in the complexes were obtained. The charge transfer is from NH_3 to AlX_3 . In NH_3 : AlF₃, the net charge on AlF_3 is -0.19and in NH_3 : AlCl₃ the net charge on $AlCl_3$ is -0.27.

IV. VIBRATIONAL ANALYSIS

In order to provide a basis for statistical mechanical calculations of the thermodynamic functions of the NH_3 : AlX_3 complexes (X = F, Cl, Br), the observed vibrational frequencies for gaseous NH_3 : $AlCl_3$ and NH_3 : $AlBr_3$ were used to derive a self-consistent set of force constants, which could then be extrapolated and interpolated to produce a complete set of vibrational frequencies for each of the three gaseous complexes. The details of these analyses are described in the following parts of this section.

A. Internal coordinates and symmetry coordinates

Pictorial sketches of the staggered and eclipsed configurations used to define the internal coordinates are shown as inserts *b* and *c* in Fig. 3. The specific internal coordinates used to construct the symmetry coordinates were the Al-N, Al-X, and N-H bonds and the X-Al-X, X-Al-N, H-N-Al, and H-N-H angles. The values of the interatomic distances and bond angles associated with each internal coordinate type in each gaseous NH_3 : AlX₃ complex are listed in Table III, together with references to the source of the values. (In the vibrational analysis, experimental values were used for X = Cl and Br, MO calculated values were used for X = F.)

For the eight-atom NH_3 : AlX_3 species with $C_{3\nu}$ symmetry and either staggered or eclipsed configuration as shown in Fig. 3, the vibrational representation is given by Eq. (4). The contributions of each of the internal

coordinate sets to the symmetry species A_1 , A_2 , and Ein C_{3v} for either configuration are as follows: The N-H, Al-X, H-N-H, H-N-Al, N-Al-X, and X-Al-X coordinates each contribute once to A_1 and once to E, the Al-N coordinate contributes once to A_1 , and none of the coordinates contribute to A_2 . This set of internal coordinates leads to two redundancies in the A_1 block, but it is necessary to employ such a set in order to provide a complete description of the E modes. Since the torsional frequency (A_2) cannot be observed in the IR or Raman, or inferred from other data, a torsional coordinate is not included in this analysis. Instead, in order to provide a complete set of vibrational frequencies for the thermodynamic calculations, a range of estimated values is used as discussed in Secs. IVD and V. The complete set of symmetry coordinates (including redundant coordinates) for the NH₃: AlX₃ molecule (staggered or eclipsed) is listed below:

A₁ block

$$S_{1}(A_{1}) = \frac{1}{\sqrt{3}} [r(1,7) + r(2,7) + r(3,7)]$$

$$S_{2}(A_{1}) = \frac{1}{\sqrt{3}} [\alpha(2,7,3) + \alpha(1,7,3) + \alpha(1,7,2)]$$

$$S_{3}(A_{1}) = \frac{1}{\sqrt{3}} [r(4,8) + r(5,8) + r(6,8)]$$

$$S_{4}(A_{1}) = \frac{1}{\sqrt{3}} [\beta(5,8,6) + \beta(4,8,6) + \beta(4,8,5)]$$

$$S_{5}(A_{1}) = [r(7,8)]$$

$$S_{6}(A_{1}) = \frac{1}{\sqrt{3}} [\gamma(4,8,7) + \gamma(5,8,7) + \gamma(6,8,7)]$$

$$S_{7}(A_{1}) = \frac{1}{\sqrt{3}} [\delta(1,7,8) + \delta(2,7,8) + \delta(3,7,8)]$$

E block

$$S_{1}(E) = \frac{1}{\sqrt{6}} \left[2r(1,7) - r(2,7) - r(3,7) \right]$$

$$S_{2}(E) = \frac{1}{\sqrt{6}} \left[2r(4,8) - r(5,8) - r(6,8) \right]$$

$$S_{3}(E) = \frac{1}{\sqrt{6}} \left[2\alpha(2,7,3) - \alpha(1,7,3) - \alpha(1,7,2) \right]$$

$$S_{4}(E) = \frac{1}{\sqrt{6}} \left[2\beta(5,8,6) - \beta(4,8,6) - \beta(4,8,5) \right]$$

$$S_{5}(E) = \frac{1}{\sqrt{6}} \left[2\gamma(4,8,7) - \gamma(5,8,7) - \gamma(6,8,7) \right]$$

$$S_{6}(E) = \frac{1}{\sqrt{6}} \left[2\delta(1,7,8) - \delta(2,7,8) - \delta(3,7,8) \right]$$

$$S_{7}(E) = \frac{1}{\sqrt{2}} \left[r(2,7) - r(3,7) \right]$$

$$S_8(E) = \frac{1}{\sqrt{2}} [r(5,8) - r(6,8)]$$

$$S_9(E) = \frac{1}{\sqrt{2}} [\alpha(1,7,3) - \alpha(1,7,2)]$$

$$S_{10}(E) = \frac{1}{\sqrt{2}} [\beta(4,8,6) - \beta(4,8,5)]$$

$$S_{11}(E) = \frac{1}{\sqrt{2}} [\gamma(5,8,7) - \gamma(6,8,7)]$$

$$S_{12}(E) = \frac{1}{\sqrt{12}} [\delta(2,7,8) - \delta(3,7,8)]$$

where the symbols γ , α , β , γ , and δ refer to internal coordinates defined in Fig. 3. The numbers in parentheses refer to the specific atoms forming each internal coordinate, following the numbering system in Fig. 3. By judicious numbering of the hydrogen and halogen atoms in the eclipsed and staggered configurations as given in Fig. 3, the symmetry coordinates listed above can be applied to both configurations.

B. The kinetic and potential energy matrices

The vibrational analysis was conducted using the conventional $FG - E\lambda = 0$ matrix method (described, e.g., by Nakamoto^{21(b)}). Symmetrized *G*-matrices for each molecule (X = F, Cl, Br) in both configurations (eclipsed and staggered) were constructed using the known masses of the atoms, the geometric parameters in Table III, and the symmetry coordinates given above. The symmetrized *G*-matrix elements were calculated with the computer program GMAT.²⁸ Based on the set of symmetry coordinates selected in this analysis, the *G*-matrix elements for the staggered and eclipsed configurations are identical.

The potential function used to construct the F matrix was based on a valence force field which consisted of a principal valence force constant for each of the internal coordinates defined in Fig. 3 together with selected bond/bond, bond/angle, and angle/angle interaction terms. During early calculations, all symmetrized Fmatrix elements were tested to determine which interaction parameters had the greatest positive impact on the fit between observed and calculated frequencies. In order to obtain a reasonable fit, it was found necessary to include several of the bond/bond interactions involving a common atom as well as bond/angle and angle/ angle terms involving a common bond. However, to assure that the number of adjustable force parameters was not greater than the number of observed frequencies, the force field was developed using an adjustment procedure that is currently being tested (with good success) on a variety of simple and complicated molecules.²⁹ This procedure, called the adjusted valence force field (AVFF), considers the bond/bond and bond/angle interactions around a nonterminal atom (the nitrogen and aluminum atoms in the present case) and describes their values as a weighted fraction of the average value of the corresponding principal valence force constants. Specifically, the interaction parameter k_{ij} between two bonds, i and j, sharing a common atom is given by the

expression $k_{ij} = f(K_i + K_j)/2$; the interaction parameter h_{ik} between a bond *i* and an angle *k* (where *i* is one side of *k*) is given by $h_{ik} = f(K_i + H_k)/2$; and the interaction between an angle *k* and an angle *l* having a common bond and the same center atom is given by $h'_{kl} = f(H_k + H_l)/2$. (The K's and H's are the corresponding valence force constants.) The rational and justification for this AVFF approach are discussed further in part D of this section and in Ref. 29.

Further, while satisfactory fits of observed and calcu-

lated frequencies could be obtained with the above described force field, precise matching of the H-N-H bending modes required the inclusion of a small additional H-N-H/H-N-H angle/angle interaction. The introduction of this particular interaction parameter to the AVFF has been found to be necessary in almost all cases where terminal hydrogen atoms are involved (e.g., NH_3 , CH_4 , SiH_4 , GeH_4).

Finally then, the set of force constants that result from the AVFF assumptions is defined as follows:

$$\begin{split} &K_{\rm NH} = K_1 = {\rm N-H} \text{ stretching constant} \\ &K_{\rm A1X} = K_2 = {\rm Al-X} \text{ stretching constant} \\ &K_{\rm A1N} = K_3 = {\rm Al-N} \text{ stretching constant} \\ &H_{\rm HNH} = H_4 = {\rm H-N-H} \text{ bending constant} \\ &H_{\rm XA1X} = H_5 = {\rm X-Al-X} \text{ bending constant} \\ &H_{\rm XA1X} = H_5 = {\rm X-Al-X} \text{ bending constant} \\ &H_{\rm HNA1} = H_7 = {\rm H-N-Al} \text{ bending constant} \\ &H_{\rm HNA1} = H_7 = {\rm H-N-Al} \text{ bending constant} \\ &H_{\rm HNA1} = H_7 = {\rm H-N-Al} \text{ bending constant} \\ &h_{\rm HNH,I} = H_8 = \text{ supplemental } {\rm H-N-H/H-N-H} \text{ angle/angle interaction parameter} \\ &k_{\rm NH,INH} = f_1 \cdot K_1 = {\rm N-H/N-H} \text{ bond/bond interaction constant} \\ &k_{\rm A1X}/{\rm A1X} = f_2 \cdot K_2 = {\rm Al-X/Al-X} \text{ bond/bond interaction constant} \\ &k_{\rm A1X/A1N} = \left(\frac{f_1}{2}\right) \cdot (K_1 + K_3) = {\rm N-H/Al-N} \text{ bond/bond interaction constant} \\ &h_{\rm NH/H} = \left(\frac{f_1}{2}\right) \cdot (K_1 + H_4) = {\rm N-H/H-N-H} \text{ bond/angle interaction constant} \\ &h_{\rm NH/HNH} = \left(\frac{f_1}{2}\right) \cdot (K_1 + H_4) = {\rm N-H/H-N-Al} \text{ bond/angle interaction constant} \end{split}$$

 $h_{A1X/XA1X} = \left(\frac{f_2}{2}\right) \cdot (K_2 + H_5) = A1 - X/X - A1 - X$ bond/angle interaction constant

 $h_{A_{1N}/NA_{1X}} = \left(\frac{f_2}{2}\right) \cdot (K_3 + H_6) = Al - N/N - Al - X$ bond/angle interaction constant

 $h_{A1N/HNA1} = \left(\frac{f_1}{2}\right) \cdot (K_3 + H_7) = A1 - N/H - N - A1$ bond/angle interaction constant

 $h_{A_{1X}/NA_{1X}} = \left(\frac{f_2}{2}\right) \cdot (K_2 + H_6) = Al - X/N - Al - X$ bond/angle interaction constant $h'_{BNH/HNH} = f_1 \cdot H_4 = H - N - H/H - N - H$ angle/angle interaction constant

 $h'_{XA1X/XA1X} = f_2 \cdot H_5 = X - Al - X/X - Al - X$ angle/angle interaction constant

 $h'_{XA1X/NA1X} = \left(\frac{f_2}{2}\right) \cdot (H_5 + H_6) = X - Al - X/N - Al - X$ angle/angle interaction constant $h'_{NA1X/NA1X} = f_2 \cdot H_6 = N - Al - X/N - Al - X$ angle/angle interaction constant $h'_{HNH/HNA1} = \left(\frac{f_1}{2}\right) \cdot (H_4 + H_7) = H - N - H/H - N - Al$ angle/angle interaction constant $h'_{HNA1/HNA1} = f_1 \cdot H_7 = H - N - Al/H - N - Al$ angle/angle interaction constant.

These force constants were assembled in an unsymmetrized F matrix which was then symmetrized using the previously listed symmetry coordinates. The resulting symmetrized F-matrix elements are

 $F_{11} = K_1 \cdot (1 + 2f_1)$ $F_{12} = r_1 \cdot f_1 \cdot (K_1 + H_4)$ $F_{15} = \left(\frac{\sqrt{3} \cdot f_1}{2}\right) \cdot (K_1 + K_3)$ $F_{17} = \left(\frac{r_3 \cdot f_1}{2}\right) \cdot (K_1 + H_7)$ $F_{22} = r_1^2 \cdot H_4 \cdot (1 + 2f_2)$ $F_{27} = r_1 \cdot r_3 \cdot f_1 \cdot (H_4 + H_7) + 2 \cdot r_1 \cdot r_3 \cdot H_8$ $F_{33} = K_2 \cdot (1 + 2f_2)$ $F_{34} = r_2 \cdot f_2 \cdot (K_2 + H_5)$ $F_{35} = \left(\frac{\sqrt{3} \cdot f_2}{2}\right) \cdot (K_2 + K_3)$ $F_{36} = \left(\frac{r_3 \cdot f_2}{2}\right) \cdot (K_2 + K_6)$ $F_{44} = r_2^2 \cdot H_5 \cdot (1 + 2f_2)$ $F_{46} = r_2 \cdot r_3 \cdot f_2 \cdot (H_5 + H_6)$ $F_{55} = K_3$ $F_{56} = \left(\frac{\sqrt{3} \cdot r_2 \cdot f_2}{2}\right) \cdot (K_3 + H_6)$ $F_{57} = \left(\frac{\sqrt{3} \cdot r_1 \cdot f_1}{2}\right) \cdot (K_3 + H_7)$ $F_{66} = r_2 \cdot r_3 \cdot H_6 \cdot (1 + 2f_2)$ $F_{77} = r_1 \cdot r_3 \cdot H_7 \cdot (1 + 2f_1)$

E block

$$F_{11} = K_1 \cdot (1 - f_1)$$

$$F_{12} = -\left(\frac{r_1 \cdot f_1}{2}\right) \cdot (K_1 + H_4)$$

$$F_{16} = \left(\frac{r_3 \cdot f_1}{2}\right) \cdot (K_1 + H_7)$$

$$F_{22} = r_1^2 \cdot H_4 \cdot (1 - f_1)$$

$$F_{26} = -\left(\frac{r_1 \cdot r_3 \cdot f_1}{2}\right) \cdot (H_4 + H_7)$$

$$F_{33} = K_2 \cdot (1 - f_2)$$

$$F_{34} = -\left(\frac{r_2 \cdot f_2}{2}\right) \cdot (K_2 + H_6)$$

$$F_{35} = \left(\frac{r_3 \cdot f_2}{2}\right) \cdot (K_2 + H_6)$$

$$F_{44} = r_2^2 \cdot H_5 \cdot (1 - f_2)$$

$$F_{45} = -\left(\frac{r_2 \cdot r_3 \cdot f_2}{2}\right) \cdot (H_5 + H_6)$$

$$F_{55} = r_2 \cdot r_3 \cdot H_6 \cdot (1 - f_2)$$

TABLE V. Adjusted valence force field derived for the molecules $NH_3:AlX_3$ (X = F, Cl, Br).

Force constant ² (mdyn/Å)	NH ₃ : AlF ₃	NH ₃ :AlCl ₃	NH ₃ : AlBr ₃
N-H STR/K _{NH}	6,25	6.25	6.25
H-N-H BND/H _{HNH}	0.60	0,59	0.58
H-N-Al BND/H _{HNA1}	0.14	0.14	0.14
$f_1(AlNH_3)^b$	0.009	0.009	0,009
HNH Int. /h"	0.053	0.053	0.053
A1-N STR/KAIN	1.61	1,50	1.45
Al-X STR/ K_{Alx}	4,33	2.34	1.97
X-Al-X BND/H _{XAIX}	0.18	0.093	0.083
N-A1-X BND/HNAIX	0.28	0.23	0.195
$f_2(NA1X_3)^b$	0,017	0.08	0,08

 a STR = stretch, BND = bend, H-N-H Int = HNH/HNH interaction. ^bUnitless.

$$F_{66} = r_1 \cdot r_3 \cdot H_7 \cdot (1 - f_1)$$

where $r_1 = r_{N-H}$, $r_2 = r_{A1-X}$, and $r_3 = r_{A1-N}$.

C. The normal coordinate analysis

The steps taken in the normal coordinate analysis were as follows: Initially, the set of eight independent valence force constant values and the two weighting factors $(f_1 \text{ and } f_2)$ were determined for NH₃: AlCl₃ using ten observed or inferred frequencies (Raman and infrared) for that complex. (These calculations were performed with the computer program FPERT.²⁸ Next, sets of force constant and f values were determined for NH₃: AlBr₃. However, since there are only seven observed or inferred frequencies for NH3: AlBr3, and since the force constants for the NH₃ part of the complex are expected to be relatively invariant to change of halide. values for five of the ten adjustable parameters were derived by other means described below, and held fixed in the force constant calculation. Finally, the sets of valence force constants and f values for NH₃: AlCl₂ and NH₃: AlBr₃ were used to establish an approximate force constant set for NH₃: AlF₃.

In the case of NH_3 : AlCl₃, the ten observed frequencies were fit exactly by the assumed force field as is shown in Table IV. The iteratively derived force constants and f values that produced the calculated frequencies are listed in Table V and are discussed more fully in part D of this section.

As was mentioned above, only five of the ten force parameters for NH_3 : $AlBr_3$ were adjusted in the iteration step. The K_{A1N} value for NH_3 : $AlBr_3$ (and for NH_3 : AlF_3 as well) was derived by a procedure that involved use of the empirical electronegativity-based relationship for bond stretching force constants derived by Gordy³⁰ over 30 yrs ago, a method for calculating group electronegativities reported by Huheey, ³¹ and information on charge distribution within the NH_3 : AlF_3 and NH_3 : $AlCl_3$ complexes obtained from the molecular orbital calculations discussed in Sec. III. The Gordy relationship is

$$K_{AB} = 1.67 N \left(\frac{\chi_A \chi_B}{d_{AB}^2}\right)^{3/4} + 0.3,$$
 (5)

TABLE VI. Summary of group electronegativity calculations for the NH_3 : AlX₃ complexes (X = F, Cl, Br).

Complex	Group, i	δ _i	x_i^P	K _{A1N} , mdyn/Å
$NH_3: AlF_3$	${ {\rm NH}_3 \atop {\rm A1F}_3 }$	$+0.19^{a}$ 0.19 ²	2.74) 2.54)	1.61°
NH ₃ : AlCl ₃	∫NH ₃ AlCl ₃	+ 0. 27 ^a - 0. 27 ^a	2.83) 2.20)	1.50 (N = 0.52)
$NH_3: AlBr_3$	{NH ₃ AlBr ₃	(+ 0, 35) ^b (- 0, 35) ^b	2.92 2.02	1.45 ^c

^aDerived from STO-3G MO calculations. ^bEstimated.

^cCalculated using the Gordy equation with the value of N derived from the computed value of K_{A1N} for the NH₃: AlCl₃ complex.

where K_{AB} is the generalized valence force constant for the A-B bond in mdyn/Å; χ_A and χ_B are, respectively, the Pauling electronegativities of the bonded atoms; d_{AB} is the A-B bond distance in angstroms and N is the bond order. Instead of using the Pauling electronegativities for nitrogen and aluminum, a group electronegativity value was developed for the NH₃ group and each AlX₃ group (X = F, Cl, Br) via the method of Huheey.³¹ The details of the group electronegativity calculation are given in Huheey's paper and will not be repeated here. It is important to mention, however, that the electronegativity values $\chi^{\rm H}$ computed by the Huheey method were converted to the Pauling scale $\chi^{\rm P}$ using the relationship

$$\chi^{\rm P} = 0.336 \chi^{\rm H} - 0.208 . \tag{6}$$

This relationship was obtained by least-squares fitting of a plot of Pauling vs Huheey values as given in Table II of Huheey's paper.³¹ The group electronegativity relationships derived in this manner and adjusted to the Paul ing scale are given by

$$\chi^{\rm P}_{\rm NH_2} = 2.53 + 1.12\delta_{\rm NH_2} , \qquad (7)$$

$$\chi^{\rm P}_{\rm A1F_2} = 2.\ 72 + 0.\ 96\delta_{\rm A1F_3},\tag{8}$$

$$\chi^{\rm P}_{\rm A1C1_3} = 2.40 + 0.76\delta_{\rm A1C1_3} , \qquad (9)$$

$$\chi^{\rm P}_{\rm A1Br_g} = 2.25 + 0.67 \delta_{\rm A1Br_3} , \qquad (10)$$

where δ_i is the fractional charge of group *i* in the respective molecule. The values of the fractional charges are listed in Table VI together with the results of the group electronegativity and K_{AIN} calculations. Since the Al-N bond lengths in all three of the NH₂; AlX₂ complexes are essentially the same, the assumption was made that the bond order (N = 0.52) derived by application of Eq. (5) to the iteratively obtained K_{A1N} value for NH_3 : AlCl₃ was the same for all three complexes. Further, the estimated δ_i values for the NH₃ and AlBr₃ groups in NH₃: AlBr₃ were obtained by a simple linear interpolation of the values for these groups in NH₃: AlCl₃ and NH_3 : AlF₃. As can be seen from Eqs. (7) and (10), the group electronegativities for NH3 and AlBr3 are not overly sensitive to uncertainties in fractional charge when these uncertainties are less than or equal to a tenth of a charge unit, which is likely the case with our estimated values.

One of the motivations for work that is currently going on to explore the AVFF approach is the desire to develop a reasonably transferable set of "generalized" valence force constants for submolecular units such as the NH₃ group in the NH₃: AlX₃ complexes. In this light, it seemed advantageous to hold constant the force constants and weighting factor localized around the NH₃ group. In the actual calculations for NH₃: AlBr₃, f_1 , $H_{\rm HNA1}$, and $h''_{\rm HNH/HNH}$ were held fixed but $K_{\rm NH}$ and $H_{\rm HNH}$ were varied to "fine tune" the final set of calculated frequencies. (As the final results show, however, there was hardly any adjustment in these latter two force constants.) Further since f for gaseous AlBr₃ turned out to be equal to f for gaseous AlCl₃ (see Table VII), the same value of f_2 determined for NH₃: AlCl₃ was applied to NH₃: AlBr₃.

With the derived values of K_{A1N} , f_1 , f_2 , H_{HNA1} , and $h''_{HNH/HNH}$ for NH₃: AlBr₃ held fixed, the remaining five force parameters were then adjusted to give the best fit to the seven observed NH₃: AlBr₃ frequencies. The results of these calculations, which may be found in Tables IV and V, again show excellent correlation of observed

TABLE VII. Comparison of GVFF and AVFF force constants (in mdyn/Å) for AlF₃, AlCl₃, AlBr₃, and NH₃. (All force constant sets fit the observed frequencies within ± 1.5 cm⁻¹.)

Force constant	AlF ₃ ^a		AlCl ₃ ^b		AlBr ₃ ^a		NH ₃ ^c	
	GVFF	AVFF	GVFF	AVFF	GVFF	AVFF	GVFF	AVFF
K,	4.64	4.67	2.49	2.67	2,16	2,26	6,35	6.36
Hα	0.176	0.175	0.10	0.09 ₁	0.08 ₃	0.07 ₆	0.54	0.54
k	0.04	• • •	0.21	•••	0.167	•••	0.04 ₁	•••
haa	• • •	• • •	•••	•••	•••	•••	- 0.06 ₂	-0.062
^h ra	•••	• • •	-0.043	•• •	•••	•••	•••	•••
rd.	•••	0.0095	•••	0.045	•••	0.045	•••	0.006

^aNatural abundance masses used; three frequencies fit.

^bCalculations for Cl³⁵ and Cl³⁷ isotopes; six frequencies fit.

 $^{\rm c}$ Calculations for N¹⁴ and N¹⁶ isotopes; seven frequencies fit.

^dUnitless parameter.



FIG. 4. A correlation of selected bond stretching and angle bending force constants derived from the vibrational analysis of observed frequencies and from the STO-3G molecular orbital calculations.

and calculated frequencies, band assignments, and force constant values.

Next, using the iteratively computed force constants and f values for the chloride and bromide complexes, a set of estimated force constants was developed for NH_3 : AlF₃. For the force constants and f value arising from the NH₃ part of the complexes, the trend in values on going from bromide to chloride was extended to the fluoride by a simple linear extrapolation. The value of $K_{A 1N}$ for the fluoride complex was determined in the manner outlined above and in Table VI. The value of K_{A1F} was taken from the plot of Fig. 4, where MO calculated force constants for N-H, Al-X, and Al-N bonds in the NH_3 : AlX₃ complexes and in gaseous AlF₃, NH_3 , and AlCl₃ are compared to iteratively determined force constants, using the observed frequencies in each case. Although the MO computed force constants are consistently greater than the frequency-derived values, the correlation appears to be nearly linear above MO values of ~2 mdyn/Å.

Because the plot in Fig. 4 has little precision below ~ 1 mdyn/Å (MO scale), it is not considered suitable for making predictions about bending force constants. Instead, H_{FA1F} was set equal to twice H_{C1A1C1} based on the finding that the F-Al-F bending constant in gaseous AlF₃ is very nearly twice the Cl-Al-Cl bending constant in gaseous AlF₃ is very nearly twice the Cl-Al-Cl bending constant in gaseous AlF₃ is very nearly twice the Cl-Al-Cl bending constant in gaseous AlF₃ is very nearly twice the Cl-Al-Cl bending constant in gaseous AlCl₃ (Table VII). Values of $K_{\rm NH}$, $H_{\rm NA1X}$, and $H_{\rm HNH}$ for NH₃: AlF₃ were obtained by extrapolation of the trend on going from NH₃: AlBr₃ to NH₃: AlCl₃ since there was no other obvious basis for their derivation. The value of f_2 for the AlF₃ group in NH₃: AlF₃ was determined from values for gaseous AlCl₃ (f=0.045) NH₃: AlCl₃ ($f_2=0.08$) and gaseous AlF₃ (f=0.0095) using the following ratio:

$$\frac{f_2(\mathrm{NH}_3:\mathrm{AlF}_3)}{f(\mathrm{AlF}_3)} = \frac{f_2(\mathrm{NH}_3:\mathrm{AlCl}_3)}{f(\mathrm{AlCl}_3)} \ .$$

The resulting force constants for NH_3 : AlF_3 are listed in Table V and the corresponding sets of "calculated" frequencies are given in Table IV.

D. Comments on the vibrational analysis

It is worthwhile at this point to evaluate and comment on three aspects of the vibrational analysis, i.e., the sensibility of the AVFF applied in the above calculations, the assignments of the observed and calculated frequencies, and the range of plausible values for the unobserved torsional mode.

In the application of the AVFF to other molecules (e.g., NH₃, AlF₃, AlCl₃, and AlBr₃, see Table VII), the principal valence force constant values are always within 10% of the GVFF values—the more covalent the bond(s) involved the closer the agreement between the GVFF and AVFF values. Also, in many cases involving molecules with a single nonterminal atom, the AVFF, with its valence force constants and single f value, gives as good a fit to observed frequencies as a GVFF with the same valence force constants plus several additional interaction parameters.²⁹ This is undoubtedly due to the fact that the AVFF provides a means of including certain offdiagonal interactions that are often omitted in the application of a GVFF. The transferability of the " NH_3 : Al" localized force constants from NH₃: AlCl₃ to NH₃: AlBr₃ is certainly an encouraging feature of this particular application of the AVFF. More detailed inspection of the AVFF as it compares to the GVFF and other force fields will be presented in another publication.²⁹ A sample of the type of results obtained for molecules relevant to this study has already been illustrated in Table VII.

The correlations between frequency and principal internal coordinate in Table IV are all in conscnance with expectation. Uncertainties in the positions of the unobserved H-N-H bending modes should not have a significant effect on the thermodynamic calculations because their contribution to the entropy term is small compared to that of the low frequency modes. The most critical aspect of the normal coordinate analysis results is the degree of correctness of the predicted values for the unobserved low-frequency E modes.

For the purposes of the thermodynamic analyses which follow, it is still necessary to know the value of the Raman and infrared inactive torsional (A_2) mode for each complex. A handle on this is gotten by examination of published torsional frequencies for related molecules. Published values for torsional frequencies of ethane and ethane-like molecules are listed in Table VIII.

TABLE VIII. Torsional frequencies for ethane and selected ethane-like molecules.

Molecule	Torsional frequency	Reference
CH ₃ CH ₃	289 cm^{-1}	32
CH ₃ CD ₃	253 cm^{-1}	32
CH ₃ CH ₂ Cl	251 cm^{-1}	33
CH ₃ CH ₂ Br	249 cm^{-1}	33
CH ₃ CH ₂ I	230 cm^{-1}	33
CD_3CD_3	208 cm^{-1}	32
CCl ₃ CCl ₃	61 cm^{-1}	34
CBr ₃ CBr ₃	51 cm^{-1}	34

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Complex	Calculated ^a from frequencies in Table IV (700 K)	Experimental
NH ₃ :AlF ₃	28.6±0.8	0 0 0
NH ₃ : AlCl ₃	28.2 ± 0.8	36.2 ± 1.9^{b} 28.8 ± 2.2 ^c
$NH_3: AlBr_3$	28.4 ± 0.8	33,7 \pm 1,5 ^d

TABLE IX. Entropy changes (cal mol⁻¹ deg⁻¹) for the reaction $NH_3:AIX_3(g) \rightleftharpoons NH_3(g) + AIX_3(g)$.

^aAn estimated torsional frequency of 150 cm⁻¹ was used. The upper uncertainty limit corresponds to a torsional frequency of 225 cm⁻¹ and the lower limit to 100 cm⁻¹.

^bReference 4 (at 653 K).

°Reference 37 (at 723 K).

^dReference 5 (at 723 K).

Based on (1) the magnitude of the values in Table VIII, (2) the observation that substitution of Br for Cl has only a small effect on the torsional frequency, and (3) the finding that the MO-calculated value of the torsional mode for NH₃: AlF₃ is 149 cm⁻¹ (see Table IV), it is deduced that the actual torsional modes of NH₃ : AlX₃ (X = F, Br, and Cl) could conceivably lie anywhere between 100 and 225 cm⁻¹. The upper limit of 225 cm⁻¹ is set at a somewhat lower value than the highest frequencies in Table VIII by virtue of the fact that the MO calculated torsional mode of NH₃ : AlF₃ is lower than the torsional frequencies for any of the hydrogen-bearing substituted ethanes in Table VIII. Accordingly, values of 100, 150, and 225 cm⁻¹ are used in the thermodynamic calculations described in the next section.

V. THERMODYNAMIC FUNCTIONS

The measured and calculated frequencies for NH_3 : $AlCl_3$ and NH_3 : $AlBr_3$, as well as the estimated frequencies for NH_3 : AlF_3 (Table IV), were used in a statistical mechanical calculation³⁵ of the entropy change for the NH_3 : AlX_3 dissociation reaction [reaction in Eq. (2)]. Frequencies for NH_3 , $AlCl_3$, and $AlBr_3$ were taken from Table I and frequencies for AlF_3 were taken from the JANAF Tables. ³⁶ Structural data required for the calculation of the products of the moments of inertia were taken from the experimental and theoretical parameters given in Table III for the complexes and from the JANAF Tables for NH_3 , AlF_3 , $AlCl_3$, and $AlBr_3$. The entropy changes for the reaction in Eq. (2) at 700 K are given in Table IX. The entropies for the staggered and eclipsed forms based on the frequencies are of course the same because the A_1 and E modes are independent of conformation by virtue of the internal coordinates used and the conformational dependence of the torsional mode is essentially indeterminate. The calculated dissociation entropies are between 28 and 29 cal mol⁻¹ deg⁻¹ with no apparent dependence on the halide involved. The decrease in entropy due to lower frequencies for $F \rightarrow Br$ is offset by an increase in the rotational entropy due to the mass effect. Experimentally measured ΔS values are also given in Table IX. For NH₃: AlCl₃ Shubaev³⁷ reports $\Delta S = 28.8$ cal mol⁻¹ deg⁻¹, while Laughlin and Gregory⁴ report ΔS = 36.2 cal mol⁻¹ deg⁻¹. The calculated ΔS based on the vibrational frequencies are in closer agreement with the results of Shubaev than those of Laughlin and Gregory.

The enthalpy data for the reaction in Eq. (2), with $X = Cl^{37}$ and Br, ⁵ and the enthalpy of formation at 298 K of NH₃, AlCl₃, and AlBr₃ from the JANAF Tables³⁶ were used to calculate:

 $\Delta H_{298}^{\circ}(\mathrm{NH}_3:\mathrm{AlCl}_3) = -183.4 \pm 0.9 \mathrm{kcal/mol}$,

 $\Delta H_{298}^{\circ}(\mathrm{NH}_3:\mathrm{AlBr}_3) = -143.6 \pm 2 \ \mathrm{kcal/mol}$.

For the amine fluoride, no enthalpy data for the reaction in Eq. (2) are available. The MO calculations predict a dissociation enthalpy for amine fluoride of 36.8 kcal/ mol. A scaled "experimental" value for this enthalpy of ~21 kcal/mol is obtained by comparison with theoretical and experimental³⁷ dissociation enthaplies for NH₃: AlCl₃. Using this result and the JANAF Table values for the enthalpies of formation of AlF₃ and NH₃, the resulting enthalpy of formation at 298 K for NH₃: AlF₃ is approximately – 326 kcal/mol.

The above enthalpy and entropy data, as well as, the $AlX_3(s)$ (X = F, Cl, Br) JANAF thermodynamic data, ³⁶ were used to calculate the ΔG 's for the all-gas reactions [reaction in Eq. (2)] and the gas/solid reactions.] The results are presented in Table X. Evidently, at temperatures near 700 K, the all-gas-phase reaction favors the formation of all the amine halides including the fluoride. However, because the vapor pressure of $AlF_3(s)$ is relatively low at these temperatures, no appreciable amount of the complex should form via the gasphase reaction. The gas/solid reaction does not favor the formation of the amine fluoride at 700 K. These considerations may account for the difficulties met in attempts to prepare NH₃: AlF₃. Apart from thermodynamic considerations, kinetic effects might also be of importance for this reaction.

VI. CONCLUSIONS

It is the conclusion of this study that the vibrational spectra of NH_3 : AlCl₃ and NH_3 : AlBr₃ are consistent with

TABLE X. Stabilities of the NH_3 : AIX_3 disproportionation reactions. (Data in kcal/mol.)

Reaction	Temperature	$\Delta G(X=F)$	$\Delta G(X=C1)$	$\Delta G(X=Br)$
A: $NH_3(g) + AlX_3(g) \rightarrow NH_3$: $AlX_3(g)$	700 K	- 8.0	- 15, 0	- 13, 6
	1000 K	- 3.1	- 3, 9	- 2, 5
B: $NH_3(g) + AlX_3(s) \rightarrow NH_3 : AlX_3(g)$	700 K	+29.6	-19.1	- 14.2
	1000 K	+27.1	-20.3	- 13.2

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the ethane-like, Al-N bonded structure found by Hargittai *et al.*⁸ There appears to be little resistance to internal rotation about the Al-N bond. Thermodynamic properties derived from the complete vibrational frequency sets determined for each NH₃: AlX₃ complex (X = F, Cl Br) indicate that NH₃: AlCl₃ is more stable than NH₃: AlBr₃ in the 700-1000 K temperature range. The free energy of formation of NH₃: AlF₃ from NH₃(g) and AlE (r) is expendent to be respective.

 $AlF_3(g)$ is calculated to be negative in this temperature range but is positive for the reaction of $NH_3(g)$ with $AlF_3(s)$. This result coupled with the fact that AlF_3 has a much lower vapor pressure than $AlCl_3$ and $AlBr_3$ may explain the lack of success in prior attempts to form $NH_3: AlF_3$.

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