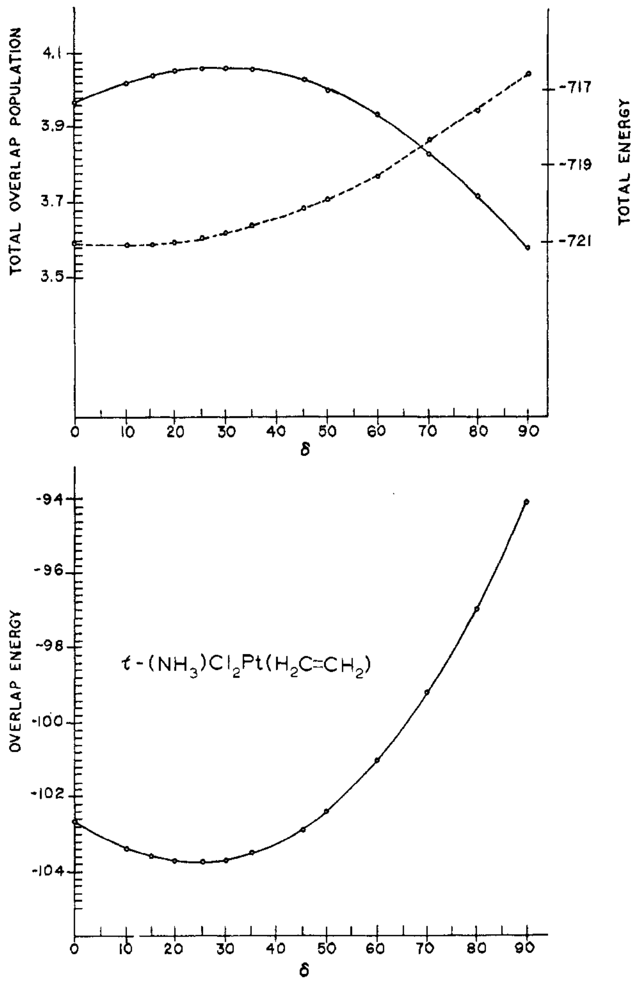

Figure 4.—Variation in total energy (– – –), total overlap population (——), and overlap energy for *trans*-(NH$_3$)PtCl$_2$(C$_2$H$_4$) as a function of δ.

Recent photoelectron spectroscopic studies of similar complexes lend partial support to our results.[13] The charge on the carbon atoms is estimated to be $-(0.4 \pm 0.1)$ for the olefinic carbon and $-(0.35 \pm 0.1)$ for the acetylenic carbon in (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and (Ph$_3$P)$_2$Pt(C$_2$Ph$_2$), respectively. In comparison, population analyses determine a computed charge for the olefinic carbon of -0.20 to -0.45 (Löwdin) or -0.74 to -0.84 (Mulliken) and for the acetylenic carbon of -0.50 to -0.66 (Löwdin) or -1.05 to -1.23 (Mulliken) as the angles δ and ω are varied. Greater negative charge on the acetylenic carbon than on the ethylenic carbon seems more reasonable since acetylene is a better π acceptor than ethylene, and acetylenes also have a greater versatility for participating in the proposed synergic mechanism.[4,5,11]

Since the structure of the molecule was kept rigid while the angle δ or ω was varied, the variation of overlap population with δ or ω may be attributed to population variations analogous to that of Blizzard and Santry.[2] Hence the population of certain orbitals definitely affects the equilibrium geometry for free or complexed acetylenes and olefins. From previous results[4,5] and calculations by other methods[2] we are inclined to ascribe this phenomenon to population of an orbital which in a higher symmetry environment could be characterized as a π-antibonding orbital of the organic moiety.

Acknowledgment.—The financial support of Esso Research Laboratories, Humble Oil and Refining Co., Baton Rouge, La., is gratefully acknowledged.

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The Proton Affinity of Borazine

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Chemical ionization mass spectrometry is a relatively new technique that has been used to provide information on the proton affinities of molecules. To date this technique has been used almost exclusively for studies of organic molecules, but it should also be adaptable to inorganic systems. Borazine, an inorganic analog of benzene, has been the subject of many theoretical and experimental investigations. We recently reported results of a chemical ionization study of borazine that indicates that the proton affinity of this molecule was in excess of 7.7 eV.[1] More quantitative measurements of the proton affinity of borazine may be relevant to both its electronic structure and its chemical properties. To establish upper and lower boundaries on the proton affinity of borazine it is necessary to observe reactions in which protonated borazine is a proton donor and other reactions in which borazine is a proton acceptor. In order to study borazine by chemical ionization methods, it is essential that the carrier gases are chemically inert with respect to borazine. Since the choice of such gaseous reagents appears to be limited, we have devised a procedure involving the study of a three component gas mixture involving a small quantity of borazine (B), a small quantity of a second proton acceptor (R), and an excess of inert carrier gas. Since a large number of ions are produced in chemical ionization reactions when two hydrocarbons are present in a gas mixture, it is advantageous for purposes of establishing reaction sequences to use partially or totally deuterated compounds for one or two of the components. Two classes of reactions investigated were (1) reactions of a proton donor with borazine through the sequence

$$\mathrm{CH_5^+ + R \longrightarrow RH^+ + CH_4}$$
$$\mathrm{RH^+ + B \longrightarrow BH^+ + R}$$

and (2) reactions of protonated borazine with a proton acceptor through the sequence

$$\mathrm{CH_5^+ + B \longrightarrow BH^+ + CH_4}$$
$$\mathrm{BH^+ + R \longrightarrow RH^+ + B}$$

These reactions involve simple transfer of a proton between stable molecules and therefore no competing process is usually possible. Haney and Franklin[2] postulated that the nonoccurrence of reactions of this type is sufficient evidence of their endothermicity.

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[1] R. F. Porter and J. J. Solomon, *J. Amer. Chem. Soc.*, **93**, 56 (1971).

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TABLE I

REACTION SEQUENCES INVOLVING BORAZINE AND PROTONATED BORAZINE

Reaction mixture	Reaction composition	Pressure range, mm	Reaction sequence	Pertinent observations	PA($H_3B_3N_3H_3$), kcal/mol
n-C_4H_{10}–$H_3B_3N_3H_3$	210:1		$C_4H_9^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_4^+$	Occurs extensively	>148 ± 1[a] or >173 ± 1[b]
C_2H_6–$H_3B_3N_3H_3$	460:1		$C_2H_4^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_4^+$	Occurs	>178 ± 0.02
CH_4–c-C_3D_6–$H_3B_3N_3H_3$	70:1.0:0.3	0.28–0.50	$CH_5^+ + c\text{-}C_3D_6 \rightarrow C_3D_6H^+$	Occurs extensively	
			$CH_5^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_4^+$	Occurs extensively	
			$C_3D_6H^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_3D^+$	Probably occurs but competes with $C_6D_{12}H^+$	
			$C_6D_{12}H^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_3D^+$	Probably occurs	>167 ± 1[c] or >186 ± 1[d]
PH_3–$H_3B_3N_3H_3$	182:1	0.25–0.51	$PH_4^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_4^+$	Occurs	>186 ± 1[e]
CD_4–c-C_3D_6–$H_3B_3N_3H_3$	146:1.0:2.8	0.56	$CD_5^+ + c\text{-}C_3D_6 \rightarrow C_3D_7^+$	Occurs extensively	
			$CD_5^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_3D^+$	Occurs extensively	
			$H_3B_3N_3H_3D^+ + C_3D_6 \rightarrow C_3D_6H^+$	Shows no reaction	>189 ± 1
CD_4–C_3H_4–$H_3B_3N_3H_3$	100:1.0:1.5	0.26–0.54	$CD_5^+ + C_3H_4 \rightarrow C_3H_4D^+$	Occurs extensively	
			$CD_5^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_3D^+$	Occurs extensively	
			$H_3B_3N_3H_3D^+ + C_3H_4 \rightarrow C_3H_5^+$	Shows no reaction	>183 ± 3[f]
CD_4–2-C_4H_6–$H_3B_3N_3H_3$	111:0.8:1.0	0.2–0.6	$CD_5^+ + C_4H_6 \rightarrow C_4H_6D^+$	Occurs extensively	
			$CD_5^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_3D^+$	Occurs extensively	
			$H_3B_3N_3H_3D^+ + C_4H_6 \rightarrow C_4H_7^+$	Shows no reaction	>198 ± 2[g]
CD_4–NH_3–$H_3B_3N_3H_3$	103:1.0:0.7	0.32–0.51	$CD_5^+ + NH_3 \rightarrow NH_3D^+$	Occurs extensively	
			$CD_5^+ + H_3B_3N_3H_3 \rightarrow H_3B_3N_3H_3D^+$	Occurs extensively	
			$H_3B_3N_3H_3D^+ + NH_3 \rightarrow NH_4^+$	Observed	<207 ± 3[h]

[a] Calculated using values for heats of formation of n-butyl ion and 1-C_4H_8. [b] Calculated using thermochemical data for *sec*-butyl ion and *trans*-2-C_4H_8 (most stable straight-chain species). [c] Calculated using thermochemical data for cyclohexane and n-$C_6H_{13}^+$ ion. [d] Calculated using thermochemical data for 1-C_6H_{12} and n-$C_6H_{13}^+$ ion. [e] Value from M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73,** 4330 (1969). [f] The heat of formation of the allyl cation was determined by using the ionization potential of the allyl radical and its heat of formation (ΔH_f(allyl, g) = 40.6 ± 1 kcal/mol): D. M. Golden, A. S. Rogers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88,** 3196 (1966). [g] Calculated using thermochemical data for n-$C_4H_7^+$ and 2-butyne. [h] Value from M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50,** 2028 (1969); data in last column unless otherwise noted taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26** (1969).

Experimental Section

The chemical ionization source used in these experiments was designed according to the description given by Field and Munson.[3] The ion box with inner dimensions of 0.438 × 0.438 in. contained a 0.002 × 0.313 in. entrance slit for the electron beam from the filament compartment and a 0.002 × 0.344 in. exit slit for the ion beam. The gas entered the source through a small stainless steel tube brazed onto the ion box. This was connected by a piece of flexible Teflon tubing to a glass inlet tube. The filament housing was external to the ion box and open to the vacuum system. The source was equipped with a repeller to maintain a field strength of 11.6 V cm^{-1}. The electron bombardment energy was maintained at 100 V and the positive ion acceleration potential was held at 3000 V. This source was found to be superior to the one described earlier.[1] Primary ions CH_3^+ and CH_4^+ from methane were completely consumed by chemical ionization reaction at a source pressure of 0.24 mm.

Gas mixtures were prepared by adding an excess of CH_4 to a bulb containing a small quantity of borazine and R, whose pressures had been measured on a silicone oil manometer. Borazine was prepared from *B*-trichloroborazine by the procedure of Hohnstedt and Haworth.[4] Methane, ethane, butane, cyclopropane-d_6, methane-d_4, allene, ammonia, and 2-butyne were obtained from commercial sources.

Results

Experimental observations of chemical ionization studies of several reaction mixtures containing borazine are summarized in Table I. Some of the more pertinent observations will be discussed briefly.

CH_4–c-C_3D_6–$H_3B_3N_3H_3$ and CD_4–c-C_3D_6–$H_3B_3N_3H_3$.—These mixtures were selected to provide a source of $C_3D_6H^+$ or $C_3D_7^+$ which could serve as D^+ donors to borazine. In the CH_4–c-C_3D_6–$H_3B_3N_3H_3$ system $C_3D_6H^+$ is formed in the reaction $CH_5^+ + C_3D_6 \rightarrow C_3D_6H^+ + CH_4$. Chemical ionization spectra of a mixture of three components and a blank of only CH_4 and C_3D_6 are shown in Table II. At high source pressures $B_3N_3H_6D^+$ and $B_3N_3H_7^+$ are the major ion species. The species $C_6D_{12}H^+$ is also observed in moderately high concentration. It was difficult quantitatively to separate the possible effect of D^+ transfer from $C_6D_{12}H^+$ to borazine from that due to D^+ transfer from $C_3D_6H^+$ to borazine. The most significant observation in the CD_4–c-C_3D_6–$H_3B_3N_3H_3$ system is that neither $B_3N_3H_6D^+$ nor $B_3N_3H_7^+$ is an effective protonating agent for c-C_3D_6. The species $B_3N_3H_7^+$ probably arises by transfer of a proton from $B_3N_3H_6D^+$

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(3) F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **87,** 3289 (1965).

(4) L. F. Hohnstedt and D. T. Haworth, *ibid.*, **82,** 89 (1960).

TABLE II

CHEMICAL IONIZATION MASS SPECTRAL DATA FOR A METHANE–CYCLOPROPANE–BORAZINE SYSTEM

CH_4-*c*-C_3D_6-$H_3B_3N_3H_3$[a]		CH_4-*c*-C_3D_6[b]	
Ion	I_i/I_t[c]	Ion	I_i/I_t
CH_5^+	2.85	CH_5^+	2.35
$C_2H_5^+$	5.69	$C_2H_5^+$	4.70
$C_3D_6H^+$	29.19	$C_3D_6H^+$	37.92
$C_3D_7^+$	3.24	$C_3D_7^+$	5.70
$H_2B_3N_3H_3^+$	4.50	$C_6D_{12}H^+$	12.08
$H_3B_3N_3H_3^+$	0.30	$C_6D_{13}^+$	2.01
$H_3B_3N_3H_4^+$	13.30	Σ(residual hydrocarbon ions)	35.23
$H_3B_3N_3H_3D^+$	7.75		
$C_6D_{12}H^+$	4.10		
$C_6D_{13}^+$	0.93		
Σ(residual hydrocarbon ions)	27.71		

[a] CH_4:*c*-C_3D_6:$H_3B_3N_3H_3$ = 70:1.0:0.3, P_s = 0.5 mm. [b] CH_4:*c*-C_3D_6 = 70:1.0, P_s = 0.51 mm. [c] Normalized intensities are given in percentages.

and/or $B_3N_3H_5^+$ to borazine. Protonation of C_3D_6 should be observed in the rise in relative intensity of $C_3D_6H^+$. The data in Table III indicate that H^+ transfer to C_3D_6 is imperceptible at source pressures of 0.56 mm.

TABLE III

CHEMICAL IONIZATION MASS SPECTRAL DATA FOR THREE-COMPONENT MIXTURES CONTAINING BORAZINE

CD_4-*c*-C_3D_6-B[a]

P_s, mm	$I_{C_3D_7^+}/I_t$[b]	$I_{C_3D_6H^+}/I_t$	$(I_{BD^+} + I_{BH^+})/I_t$	$I_{C_3D_6H^+}/I_{C_3D_7^+}$ (sample)	$I_{C_3D_6H^+}/I_{C_3D_7^+}$ (blank[c])
0.41	4.62	0.56	78.3	0.121	
0.50					0.140
0.56	2.47	0.29	90.0	0.117	0.154

CD_4-C_3H_4-B

P_s, mm	$I_{C_3H_4D^+}/I_t$	$I_{C_3H_5^+}/I_t$	$(I_{BD^+} + I_{BH^+})/I_t$	$I_{C_3H_5^+}/I_{C_3H_4D^+}$ (sample)	$I_{C_3H_5^+}/I_{C_3H_4D^+}$ (blank)
0.26	8.50	0.45	36.6	0.053	0.053
0.40	4.46	0.44	66.6	0.099	
0.45					0.112
0.54	2.83	0.32	79.8	0.113	
0.55					0.129

CD_4-NH_3-B

P_s, mm	$I_{NH_3D^+}/I_t$	$I_{NH_4^+}/I_t$	$(I_{BD^+} + I_{BH^+})/I_t$	$I_{NH_4^+}/I_{NH_3D^+}$ (sample)	$I_{NH_4^+}/I_{NH_3D^+}$ (blank)
0.32	22.3	9.0	13.2	0.404	0.290
0.51	30.7	34.7	13.4	1.13	0.736

[a] Compositions for CD_4-R-B mixtures are the same as in Table I. [b] Normalized intensities I_i/I_t are given in percentages. [c] Blank mixtures have same relative CD_4-R composition as the corresponding borazine mixture.

CD_4-C_3H_4-$H_3B_3N_3H_3$.—In this system $B_3N_3H_6D^+$ and $B_3N_3H_7^+$ increase with source pressure and constitute about 80% of the total intensity at a pressure of 0.54 mm. The most significant observation is that allene is a weaker base than borazine since the relative ion intensity of $C_3H_5^+$ which could arise by protonation of C_3H_4 from $B_3N_3H_7^+$ or from $B_3N_3H_6D^+$ is not increased at the highest source pressures.

PH_3-$H_3B_3N_3H_3$-NH_3.—In this system PH_4^+ is the predominant species formed by reaction of the primary ions with PH_3. The effect of increase in source pressure on PH_4^+ and $B_3N_3H_7^+$ is illustrated in Figure 1. The initial rate of decrease in PH_4^+ is approximately balanced by the rate of increase in $B_3N_3H_7^+$. At higher source pressures NH_4^+ appears but this is probably due to proton transfer from $B_3N_3H_7^+$ to NH_3 (see subsequent discussion). At the highest source pressures $B_3N_3H_7^+$ and NH_4^+ decrease due to further reactions leading to secondary ions (not shown in Figure 1). Assuming that the reaction $PH_4^+ + B_3N_3H_6 \rightarrow PH_3 + B_3N_3H_7^+$ is approaching equilibrium at high source pressures, we note that the K_{eq}(apparent) > 2.5×10^3 at the source temperature (375°K). This indicates that borazine is clearly a stronger base than phosphine.

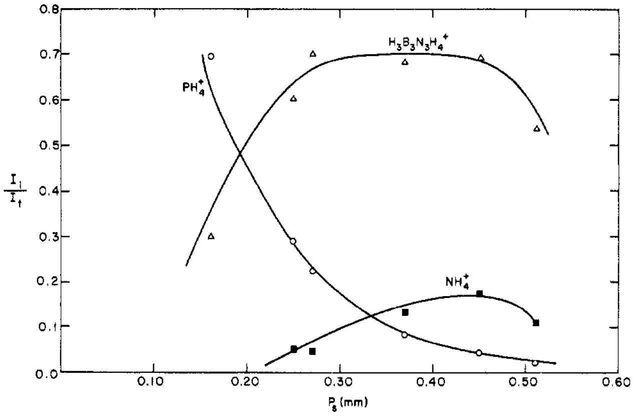

Figure 1.—Effect of source pressure on the relative intensity of the ions produced by chemical ionization of the system of phosphine, borazine, and ammonia of composition 182:1.0:trace.

CD_4-C_4H_6 (2-butyne)-$H_3B_3N_3H_3$.—Chemical ionization data for this system are summarized in Table IV. It is to be noted that the low intensity of $C_4H_7^+$ is insensitive to a relatively large increase in the ion intensities of $H_3B_3N_3H_4^+$ and $H_3B_3N_3H_3D^+$ indicating that these ions do not transfer protons to C_4H_6.

TABLE IV

CHEMICAL IONIZATION MASS SPECTRAL DATA FOR A MIXTURE CONTAINING CD_4, 2-BUTYNE, AND BORAZINE[a]

P_s	$I_{C_4H_7^+}/I_t$	$I_{C_4H_6D^+}/I_t$	$(I_{BD^+} + I_{BH^+})/I_t$	$I_{C_4H_7^+}/I_{C_4H_6D^+}$
0.2	0.87	6.93	26.21	0.126
0.38	0.55	7.75	55.86	0.071
0.42	0.63	7.74	57.51	0.081
0.55	0.54	5.66	58.26	0.095
0.60	0.59	4.69	71.43	0.126

[a] Composition 111:0.8:1.0.

CD_4-NH_3-$H_3B_3N_3H_3$.—In this system the major fraction of ion intensity is due to NH_3D^+ and NH_4^+. The relative intensities of $B_3N_3H_7^+$ are very low at high source pressures. Evidence that NH_3 is protonated by $B_3N_3H_7^+$ and $B_3N_3H_6D^+$ is noted by the increase in the NH_4^+:NH_3D^+ ratio over that due to transfer of a proton from NH_3D^+ to NH_3 (note results of blank).

Discussion

The accumulation of information on reaction sequences involving borazine as a proton acceptor and the protonated form as a proton donor (Table I) indicates that the proton affinity of borazine is greater than the proton affinity of phosphine, cyclopropane, allene, and 2-butyne but less than the proton affinity (PA) of NH_3. (PA(NH_3) = 207 ± 3 kcal/mol[5,6].) The boundary

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based on 2-butyne appears to be reliable since the thermochemical data for $C_4H_7^+$ are based upon a consistent set of measurements.[7–9] Using 198 ± 2 kcal/mol for the proton affinity of 2-butyne, we can establish limits on the proton affinity of borazine or PA(borazine) = 203 ± 7 kcal/mol. Thus borazine should be considered as a relatively strong base. It is a stronger base than benzene ($PA(C_6H_6) = 183 \pm 3$ kcal/mol).[2] It seems probable that under selected conditions the cation $B_3N_3H_7^+$ may be stabilized for further investigations.

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A Raman Study of the Hydrolysis of the Hexafluoroantimonate(1 −) Ion

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Effects of ionic solutes on water structure were examined in a recent Raman spectral investigation.[1] In that work it was necessary to establish the nature of the prominent anionic species present. In the case of sodium hexafluoroantimonate, it was not certain that SbF_6^- ions were present at all. Rate of hydrolysis studies[2] suggested that $SbF_5(OH)^-$ and $SbF_4(OH)_2^-$ ions would predominate in aqueous solution. Further, the behavior of the OH and OD stretching band contours in $NaSbF_6$ solutions[1] was significantly different from that expected if SbF_6^- were the predominant anionic species. In order to clarify the nature of the anionic species in aqueous solutions of $NaSbF_6$, Raman spectra of solid $NaSbF_6$, of $NaSbF_6$ in H_2O, and of $NaSbF_6$ in aqueous HF were obtained and are reported here.

Experimental Section

Samples of $NaSbF_6$ (98%) were obtained in polyethylene bottles from Alpha Inorganics, Inc., Beverly, Mass. Analyses of ultrafiltered aqueous solutions yielded Na:Sb:F = 1.0:1.0:(6.0 ± 0.1). Analyses for sodium and antimony were accomplished by atomic absorption spectrometry. Fluorine was determined as CaF_2 after rigorous alkaline hydrolysis.

Raman cells made of Pyrex and silica were found to be totally unsuitable for use with aqueous solutions and with solutions containing excess HF because of severe etching. Polished Raman cells fabricated from ingots of aluminum metaphosphate were used, and they were found to be ideal for the present work. Aluminum metaphosphate is colorless and it strongly resists attack even from 48% HF.[3]

Samples of solid polycrystalline $NaSbF_6$ were sealed in dry melting point tubes made of glass. No attack of the glass was noted, and Raman lines ascribable to $NaSbF_6$ only (and not to glass) were observed. In addition, the infrared spectrum from solid $NaSbF_6$ was recorded, because conflicting infrared data involving the ν_4 fundamental of SbF_6^- had been reported previously.[4–6]

Finely ground crystalline $NaSbF_6$ was examined in pellets of CsI and of KBr. Nujol mulls as well as a dispersion in a thin polyethylene film were also examined. The Christiansen effect was serious for the CsI and KBr pellets, but it was virtually eliminated by carefully grinding the $NaSbF_6$ with the other dispersants. The infrared spectra were then recorded with Beckman IR-11 and -12 instruments. The frequency error limits, 1.5 cm^{-1}, were determined mainly by absorption bandwidths.

The Raman spectra were obtained by use of a Carson Laboratories argon ion laser,[7] a Jarrell-Ash Model 25-100 double monochromator, and a noise-squaring photodetection system.[8] Polarization measurements were accomplished by use of a Polaroid sheet analyzer (HN 38), with a quartz wedge scrambler in front of the entrance slit. The optically filtered and focused beam (4880 Å, 400 mW) was passed once through the Raman cell. Scanning rates of 20 cm^{-1} min^{-1} were employed with spectral slit widths of 3.0 cm^{-1} or less and time constants of 1.5 or 2.0 sec. The dark count rate of the EMI 6256 photomultiplier tube employed was 15 sec^{-1} at −20°. The Raman displacements are accurate to ±2 cm^{-1} for sharp lines and to ±5 cm^{-1} for broad lines.

Results and Discussion

Raman and infrared spectra from dry polycrystalline $NaSbF_6$ are shown in Figure 1. Frequencies (and intensities) corresponding to Raman intensity maxima and to the infrared absorption maximum, shown in the inset, are listed and compared with corresponding values reported for $LiSbF_6$[4] and $KSbF_6$[5,6,9] in Table I. The principal frequency discrepancies evident from Table I involve the $\nu_4(F_{1u})$ fundamental. Hence, the other active fundamental is not included in Figure 1.

TABLE I

FUNDAMENTAL FREQUENCIES (CM^{-1}) OF THE SbF_6^- ION[a]

No.	Species	$NaSbF_6$[c]	$LiSbF_6$[d]	$KSbF_6$[e]
1	a_{1g}	669 (10)	668 (10)	661 (vs)
2	e_g	579 (2)	570[b] (2)	575 (s)
3	f_{1u}	672 (vs)	669 (s)	655 (vs)
4	f_{1u}	289 (s)	350 (m) (?)	284 (s)[c]
5	f_{2g}	278 (5)		278 (m)
			294 (4)	294 (m)

[a] All spectra refer to the crystalline solid. Integrated intensities in this work are listed on a scale of 10 (±20%) for Raman spectra, and qualitative infrared intensities are listed in the usual way. [b] A misprint seems to be present in the data of Table I in ref 4. Figure 2 in ref 4 suggests that 570 cm^{-1} would be a more appropriate frequency value for ν_2 in $LiSbF_6$. [c] This work. [d] Reference 4. [e] References 5 and 6.

Raman spectra from aqueous solutions of $NaSbF_6$ and from aqueous solutions of $NaSbF_6$ containing excess HF are shown in Figure 2 and the data are listed in Table II.

Spectra from Solid $NaSbF_6$.—The Raman spectrum from solid $NaSbF_6$ (Figure 1) shows the three sharp lines expected for the SbF_6^- ion (O_h point group). Site symmetry splittings are absent in contrast to the case of $KSbF_6$ where ν_5 is split into two bands.[4–6] (The spectrum was obtained with a spectral slit width of 2 cm^{-1}.)

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(7) A Carson Laboratories argon ion laser tube of BeO and a magnet from a Model 100 system were adapted for use with nonstandard electronic components. A Brewster-angle wavelength-selector prism was used instead of the usual Littrow prism.

(8) J. E. Griffiths, *Appl. Spectrosc.*, **22**, 472 (1968), and references cited therein.

(9) M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, **47**, 4159 (1969).