It is assumed that $J_{F_2H} \cong 0$, since no further splittings of the proton and PF_2 group fluorine nuclear resonances are observed. There was little change in the field position of the proton when measured at −40° indicating it is not acidic and is bonded to a carbon rather than to the oxygen atom.

F. Mass Spectra.—The mass spectrum of $(CF_3)_2C(OPF_2)I$ was obtained with the cycloid tube at room temperature and the following are the absorptions observed, given as mass number (species) and relative abundance: 12 (C^+), 1.2; 25 (CF_2^{2+}, PF^{2+}), 0.7; 28 (CO^+), 0.3; 31 (CF^+, P^+), 9.0; 47 (COF^+, PO^+), 1.6; 50 (CF_2^+, PF^+), 12.6; 63.5 (I^{2+}), 1.6; 66 (COF_2^+, POF^+), 0.8; 69 (CF_3^+, PF_2^+), 100.0; 78 ($C_2F_2O_2^+$, $COPF^+$), 2.5; 85 $(POF_2)^+$, 5.3; 88 (PF_3^+), 4.3; 97 ($C_2F_3O^+$, CF_2OP^+), 23.4; 100 ($C_2F_4^+$), 1.1; 119 ($C_2F_5^+$), 1.1; 127 (I^+), 5.5; 128 ($C_3F_4O^+$, $C_2F_3OP^+$), 1.1; 147 ($C_3F_5O^+$, $C_2F_4OP^+$), 10.4; 166 ($C_3F_6O^+$, $C_2F_5OP^+$), 1.0; 177 (CF_2I^+, PFI^+), 1.6; 196 (CF_3I^+, PF_2I^+), 14.4; 235 ($C_3F_8OP^+$), 2.3 The spectral pattern for $(CF_3)_2C(OPF_2)Br$ is: 12 (C^+), 0.9; 28 (CO^+), 1.2; 31 (CF^+, P^+), 8.8; 47 (COF^+, PO^+), 1.1; 50 (CF_2^+, PF^+), 12.2; 66 (COF_2^+, POF^+), 0.4; 69 (CF_3^+, PF_2^+), 100.0; 78 ($C_2F_2O^+$, $COPF^+$), 2.1; 79 ($^{79}Br^+$), 1.6; 81 ($^{81}Br^+$), 1.6; 85 (POF_2^+), 2.6; 88 (PF_3^+), 1.6; 97 ($C_2F_3O^+$, CF_2OP^+), 21.2; 100 ($C_2F_4^+$), 0.5; 119 ($C_2F_5^+$), 0.9; 129 ($CF_2{}^{79}Br^+$), 2.0; 131 ($CF_2{}^{81}Br^+$), 2.1; 147 ($C_3F_5O^+$, $C_2F_4OP^+$), 13.8; 148 ($CF_3{}^{79}Br^+$, $PF_2{}^{79}Br^+$), 6.4; 150 ($CF_3{}^{81}Br^+$, $PF_2{}^{81}Br^+$), 6.0; 166 ($C_3F_6O^+$, $C_2F_5OP^+$), 0.4; 179 ($C_2F_4{}^{79}Br^+$), 0.5; 181 ($C_2F_4{}^{81}Br^+$), 0.5; 207 ($C_3F_4{}^{79}BrO^+$), 0.5; 209 ($C_3F_4{}^{81}BrO^+$), 0.5; 235 ($C_3F_8OP^+$), 1.6. The pattern for $(CF_3)_2C(OPF_2)H$ has many similar features to those listed above and shows a large number of hydrogen-containing species: 12 (C^+), 0.4; 28 (CO^+), 1.0; 29 (HCO^+), 32.9; 31 (CF^+, P^+), 7.4; 47 (COF^+, PO^+), 2.4; 50 (CF_2^+, PF^+), 6.2; 51 (HCF_2, HPF^+), 40.7; 63 ($HC_2F_2^+$), 1.5; 66 (COF_2, POF^+), 0.4; 69 (CF_3^+, PF_2^+), 100.0; 78 ($C_2F_2O^+$, $COPF^+$), 1.5; 79 ($HC_2F_2O^+$, $HCOPF^+$), 33.6; 82 $(HC_2F_3)^+$, 2.0; 85 (POF_2^+), 1.6; 89 (HPF_3^+), 1.7; 93 ($C_3F_3^+$), 0.6; 97 ($C_2F_3O^+$, CF_2OP^+), 0.9; 101 ($HC_2F_4^+$), 10.7; 113 ($HC_3F_4^+$), 4.8; 128 ($C_3F_4O^+$, $C_2F_3OP^+$), 1.6; 129 ($HC_3F_4O^+$, HC_2OP^+), 9.3; 132 ($HC_3F_5^+$), 10.6; 147 ($C_3F_5O^+$, $C_2F_4OP^+$), 0.8; 167 ($HC_3F_6O^+$, $HC_2F_5OP^+$), 6.4; 217 ($HC_3F_7OP^+$), 1.2; 236 ($HC_3F_8OP^+$), 2.8.

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A Study of the Fragmentation of Trifluoromethylarsenic Compounds in the Mass Spectrometer

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The mass spectra of some trifluoromethylarsenic compounds have been examined. In addition to the products of normal fragmentation, rearranged fluorocarbon ions and species containing As–F bonds were observed in all the spectra.

Introduction

The migration, under electron impact, of groups or atoms other than hydrogen has received wide attention recently,[1] although the only relevant discussion of inorganic systems is a report of the mass spectra of perhalogeno aromatic phosphines, where the formation of rearranged fluorocarbon ions with elimination of PF_2 and PF_3 as neutral species was observed.[1a] A study of some trifluoromethyl derivatives of arsenic is described in this paper. Previous work in this field has been carried out by Cullen and Frost,[2] who measured the ionization potentials of some perfluoroarsines, and by Cowley, Burg, and Cullen,[3] who have reported a partial mass spectrum of the novel cyclic compound, $(CF_3As)_4$.

Results and Discussion

The mass spectra of compounds I–V have been examined; in each case, rearrangement ions containing As–F bonds have been found. The spectra are shown in Table I, while some metastable ions observed in the spectra, together with their assignments, are listed in Table II.

CF_3AsX_2
I, $X = H$
II, $X = Cl$

$(CF_3)_2AsX$
III, $X = H$
IV, $X = As(CF_3)_2$
V, $X = CF_3$

The initial breakdown of the dihydro compound I can be represented by the scheme shown in Figure 1, where an asterisk indicates that the appropriate metastable ion was observed. Normal fragmentation occurs by loss of H, F, or CF_3H from the molecular ion, followed by stepwise degradation of the ions so formed. However, the parent and some of the fragment ions can also lose fluorocarbon fragments containing CF or CF_2 groups, resulting in the formation of rearranged ions containing As–F bonds. For example, loss of CFH_2 and CF_2H_2 from $CF_3AsH_2^+$ gives AsF_2^+ (*m/e* 113, 1.9%)[4] and AsF^+ (*m/e* 94, 7.0%), respectively. While the corresponding metastable peak was not observed, $AsFH^+$ (*m/e* 95, 3.7%) probably arises from the molecular ion by loss of CF_2H as a neutral fragment. The formation of rearranged fluorocarbon ions

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[1] (a) J. M. Miller, *J. Chem. Soc., Sect. A*, in press; (b) J. H. Bowie, S. O. Lawesson, J. Ø. Madson, G. Schroll, and D. H. Williams, *J. Chem. Soc., Sect. B*, 951 (1966), and references therein.

[2] W. R. Cullen and D. C. Frost, *Can. J. Chem.*, **40**, 390 (1962).

[3] A. H. Cowley, A. B. Burg, and W. R. Cullen, *J. Am. Chem. Soc.*, **88**, 3178 (1966).

[4] Intensities are expressed relative to the total ionization, defined as ΣI_n where *n* refers to all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

TABLE I

MASS SPECTRA OF TRIFLUOROMETHYLARSENIC COMPOUNDS I–V

m/e	Ion	I,[4] %	m/e	Ion	I,[4] %
	I			II	
146	CF_3AsH_2	19.4	218	CF_3AsCl_2	0.6
145	CF_3AsH	1.8	216		2.6
144	CF_3As	6.1	214		4.0
127	CF_2AsH_2	2.9	181	CF_3AsCl	0.7
126	CF_2AsH	0.6	179		2.2
125	CF_2As	3.3	149	$AsCl_2$	3.0
113	AsF_2	1.9	147		19.2
107	CFAsH	0.6	145		30.5
106	CFAs	0.4	144	CF_3As	1.0
95	AsFH	3.7	131	AsClF	3.1
94	AsF	7.0	129		9.2
77	AsH_2	2.9	112	AsCl	2.2
76	AsH	11.8	110		6.4
75	As	7.3	94	AsF	2.0
69	CF_3	11.2	87	CF_2Cl	0.5
51	CF_2H	11.6	85		1.4
50	CF_2	0.5	75	As	2.9
33	CFH_2	4.6	69	CF_3	6.2
31	CF	1.9	50	CF_2	0.8
			31	CF	1.2
	III				
214	C_2F_6AsH	7.5		IV	
195	C_2F_5AsH	0.5	426	$C_4F_{12}As_2$	2.4
194	C_2F_5As	0.8	407	$C_4F_{11}As_2$	1.7
175	C_2F_4As	0.6	357	$C_3F_9As_2$	0.6
163	CF_4As	1.0	307	$C_2F_7As_2$	0.3
145	CF_3AsH	2.5	269	$C_2F_5As_2$	1.3
144	CF_3As	5.8	219	CF_3As_2	4.1
126	CF_2AsH	10.3	213	C_2F_6As	1.8
125	CF_2As	4.7	194	C_2F_5As	6.4
113	AsF_2	17.3	188	As_2F_2	0.4
95	AsFH	3.5	181	$CFAs_2$	0.3
94	AsF	6.0	175	C_2F_4As	15.6
76	AsH	1.1	169	As_2F	1.9
75	As	3.3	163	CF_4As	5.5
69	CF_3	22.0	150	As_2	4.1
51	CF_2H	10.0	144	CF_3As	5.3
50	CF_2	0.6	137	C_2F_2As	0.6
31	CF	2.1	131	C_3F_5	1.3
			125	CF_2As	4.1
	V		113	AsF_2	13.9
282	C_3F_9As	0.8	106	CFAs	2.3
263	C_3F_8As	3.5	94	AsF	5.5
194	C_2F_5As	5.2	75	As	2.5
175	C_2F_4As	3.8	69	CF_3	15.0
163	CF_4As	10.0	50	CF_2	0.8
144	CF_3As	6.0	31	CF	2.2
131	C_3F_5	2.4			
125	CF_2As	3.0			
113	AsF_2	15.6			
106	CFAs	0.7			
94	AsF	9.6			
75	As	3.8			
69	CF_3	30.9			
50	CF_2	1.3			
31	CF	3.7			

TABLE II

SOME METASTABLE IONS OBSERVED IN THE MASS SPECTRA OF TRIFLUOROMETHYLARSENIC COMPOUNDS

m/e		
Obsd	Calcd	Transition
		CF_3AsH_2 (I)
93.1	93.0	$AsFH^+ \rightarrow AsF^+ + H$
90.2	90.1	$CF_2AsH_2^+ \rightarrow CFAsH^+ + HF$
87.4	87.4	$CF_3AsH_2^+ \rightarrow AsF_2^+ + CFH_2$
60.4	60.5	$CF_3AsH_2^+ \rightarrow AsF^+ + CF_2H_2$
59.1	59.2	$AsFH^+ \rightarrow As^+ + HF$
39.5	39.6	$CF_3AsH_2^+ \rightarrow AsH^+ + CF_3H$
38.7	38.8	$CF_3AsH^+ \rightarrow As^+ + CF_3H$
18.8	18.8	$CF_2H^+ \rightarrow CF^+ + HF$
17.8	17.8	$CF_3AsH_2^+ \rightarrow CF_2H^+ + AsFH$
		$(CF_3)_2AsH$ (III)
74.2	74.2	$C_2F_6AsH^+ \rightarrow CF_2AsH^+ + CF_4$
74.0	74.0	$AsH^+ \rightarrow As^+ + H$
65.4	65.4	$C_2F_5AsH^+ \rightarrow AsF_2^+ + C_2F_3H$
38.8	38.8	$CF_3AsH^+ \rightarrow As^+ + CF_3H$
		$(CF_3)_2AsAs(CF_3)_2$ (IV)
178.6	178.3	$C_2F_5As_2^+ \rightarrow CF_3As_2^+ + CF_2$
167.5	167.6	$C_3F_8As_2^+ \rightarrow CF_4As_2^+ + C_2F_4$
88.3	88.3	$C_4F_{12}As_2^+ \rightarrow C_2F_5As^+ + (CF_3)_2AsF$
72.9	73.0	$C_2F_4As^+ \rightarrow AsF_2^+ + C_2F_2$
59.9	59.9	$C_2F_6As^+ \rightarrow AsF_2^+ + C_2F_4$
45.4	45.5	$C_2F_5As^+ \rightarrow AsF^+ + C_2F_4$
21.8	21.7	$CF_3As_2^+ \rightarrow CF_3^+ + As_2$
		$(CF_3)_3As$ (V)
133.2	133.5	$C_3F_9As^+ \rightarrow C_2F_5As^+ + CF_4$
101.0	101.0	$C_3F_8As^+ \rightarrow CF_4As^+ + C_2F_4$
72.8	73.0	$C_2F_4As^+ \rightarrow AsF_2^+ + C_2F_2$
65.9	65.8	$C_2F_5As^+ \rightarrow AsF_2^+ + C_2F_3$
65.2	65.3	$C_3F_8As^+ \rightarrow C_3F_5^+ + AsF_3$
48.5	48.6	$C_3F_8As^+ \rightarrow AsF_2^+ + C_3F_6$
45.6	45.6	$C_2F_5As^+ \rightarrow AsF^+ + C_2F_4$

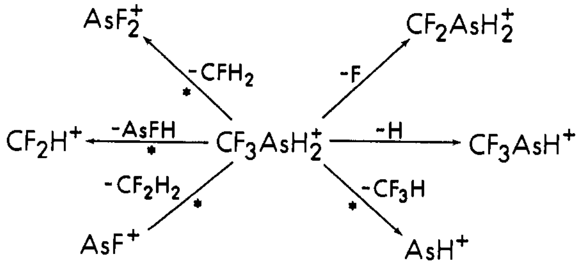


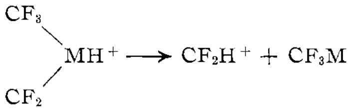
Figure 1.—Initial breakdown pattern of CF_3AsH_2.

in the spectrum (CF_2H^+ and CFH_2^+) is also characteristic of the trifluoromethylarsenic compounds examined.

The chloro derivative II did not show any metastable peaks in the mass spectrum. The most intense ion was $AsCl_2^+$, indicating that loss of CF_3 from the molecular ion is a favored process. Ions corresponding to $AsFCl^+$ were observed at m/e 131 and 129, and to CF_2Cl^+ at m/e 87 and 85. The species AsF^+ (m/e 94, 2.0%) may result from breakdown of $AsFCl^+$; AsF_2^+ was present as an ion of low intensity. In contrast, bis(trifluoromethyl)arsine (III) gave an intense peak at m/e 113 (AsF_2^+; 17.2%), which is formed from the ion $C_2F_5AsH^+$ by loss of a molecule of trifluoroethylene. As in the spectrum of the dihydro compound, rearrangement ions were observed at m/e 95 ($AsFH^+$) and m/e 94 (AsF^+). There was no metastable ion to indicate the route of formation of the abundant fluorocarbon ion, CF_2H^+ (m/e 51, 10.0%). The phosphine, $(CF_3)_2PH$, also gives an intense ion doublet at m/e 51 corresponding to CF_2H^+ and PFH^+ which can be formed from $C_2F_5PH^+$ by loss of CF_3P and C_2F_4, respectively.[5] Although the observed metastable transition in the

(5) R. C. Dobbie and R. G. Cavell, to be published.

phosphine does not identify the fragmentation, it seems reasonable to assume that formation of CF_2H^+ occurs through a similar process in both the phosphorus and arsenic compounds



$$\begin{matrix} CF_3 \\ \quad\diagdown \\ \quad MH^+ \longrightarrow CF_2H^+ + CF_3M \\ \quad\diagup \\ CF_2 \end{matrix}$$

An insufficient number of metastable peaks was observed in the spectrum of the diarsine IV to allow the complete fragmentation pattern to be deduced. It is clear from an examination of the spectrum, however, that extensive rearrangements occur here also. In addition to AsF_2^+ (*m/e* 113, 13.9%), CF_3AsF^+ (*m/e* 163, 5.5%) and $C_3F_5^+$ (*m/e* 131, 1.3%) are observed. The elimination of $(CF_3)_2AsF$ as a neutral fragment from the molecular ion is exactly paralleled in the corresponding diphosphine, where the transition

$$(CF_3)_2PP(CF_3)_2 \longrightarrow CF_3PCF_2^+ + (CF_3)_2PF$$

is found to occur.[5] It is interesting to note that the species As_2 is observed both as an ion (*m/e* 150, 4.1%) and as a neutral fragment ejected from $CF_3As_2^+$.

The breakdown pattern of tris(trifluoromethyl)-arsine (V) is shown in Figure 2. The novel feature observed in this spectrum is the formation of the ion $C_3F_5^+$ from $(CF_3)_2AsCF_2^+$ by elimination of a molecule of AsF_3, which would appear to involve the simultaneous transfer of three fluorine atoms from carbon to arsenic. Elimination of PF_3 has been noted in the mass spectrum of tris(pentafluorophenyl)phosphorus,[1a] where a metastable ion corresponding to the transition

$$(C_6F_5)_2P^+ \longrightarrow C_{12}F_7^+ + PF_3$$

has been observed.

Cowley, Burg, and Cullen[3] have recently prepared the cyclic tetramer, $(CF_3As)_4$, by the action of mercury on diiodotrifluoromethylarsine, followed by separation of the crystalline tetramer from a less volatile liquid which was not identified, although the authors considered that it might be the cyclic pentamer, $(CF_3As)_5$, by analogy with the corresponding phosphorus system.[6] We have examined the mass spectrum of the mixed product of the reaction between mercury and the diiodo compound. Peaks corresponding to the parent ions of $(CF_3As)_5$ (*m/e* 720) and $(CF_3As)_4$ (*m/e* 576) confirmed that the former was the liquid of low volatility mentioned in the literature. Metastable ions (Table III) were observed corresponding to successive loss of CF_3 and CF_2 from each parent ion. Although mass measurements were not carried out, it was evident from the $(m + 1)/m$ ratio (<1% in each case) that the ions at *m/e* 300, 225, and 150 do not contain carbon.[7] They are therefore assigned to As_4^+, As_3^+, and As_2^+. Some of the other peaks in the spectrum which could be assigned to species containing As–F bonds are shown in Table IV.

In the report of the preparation of the tetramer, $(CF_3As)_4$, the mass spectrum was given, although the ions below *m/e* 400 were not assigned.[3] It is not possible to find an ion containing As, C, and F only compatible with the molecular formula of the tetramer which will fit the observed *m/e* ratios at 318 and 299. It appears that the mass spectrum has been miscounted from *m/e* 243 through *m/e* 362, as our peaks at 1 amu higher could all be assigned satisfactorily.

While suggestions as to the mechanism of these rearrangements must remain tentative, some further observations make it appear almost certain that they are intramolecular. The possibility that species containing As–F bonds were produced by pyrolytic reactions in the heated inlet system of the mass spectrometer was dismissed by an examination of the ^{19}F nmr spectrum of compounds I, III, and V after heating at 185° for 2 hr. The only signals observed were those anticipated from the accepted structures of the compounds. Further, since no peaks above the molecular ion were observed in the mass spectra, the possibility of the formation of rearranged ions by bimolecular or ion–molecule reactions must be remote. It seems reasonable to suggest that the rearranged species are formed by intramolecular transfer of fluorine.

The results of the present study provide some insight into the thermal decomposition at 400° of tris(trifluoromethyl)arsine in which formation of the saturated fluorocarbons C_3F_8 and C_4F_{10} in addition to hexafluoroethane was reported.[8] In silica apparatus, silicon tetra-

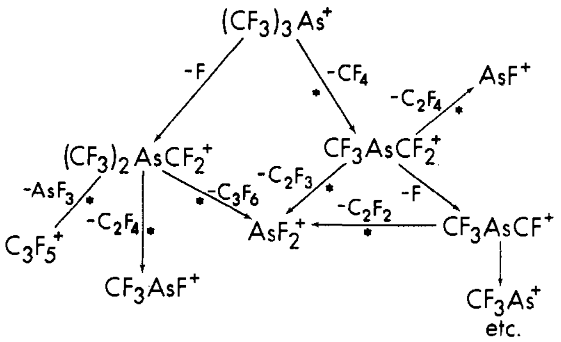


Figure 2.—Breakdown pattern of $(CF_3)_3As$.

Table III

Some Metastable Ions Observed in the Fragmentation of Cyclic Arsenic Compounds

Obsd	Calcd	Transition
588	588	$(CF_3As)_5^- \rightarrow (CF_3)_4As_5^+ + CF_3$
554	554	$(CF_3)_4As_5^+ \rightarrow (CF_3)_3As_5F^+ + CF_2$
446	446	$(CF_3As)_4^+ \rightarrow (CF_3)_3As_4^+ + CF_3$
412	412	$(CF_3)_3As_4^+ \rightarrow (CF_3)_2As_4F^+ + CF_2$

Table IV

Some Rearrangement Ions of the Cyclic Arsines Which Contain Only Arsenic and Fluorine

m/e	Ion	*m/e*	Ion
357	$As_4F_3^+$	169	As_2F^+
319	As_4F^+	113	AsF_2^+
263	$As_3F_2^+$	94	AsF^+
244	As_3F^+		

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[6] W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

[7] Natural carbon contains 1.1% of the ^{13}C isotope.

[8] P. B. Ayscough and H. J. Emeléus, *J. Chem. Soc.*, 3381 (1954).

fluoride and carbon dioxide were formed, whereas in a platinum vessel arsenic trifluoride and a polymer (polytetrafluoroethylene) were observed. We feel that this is good evidence for primary formation of CF_2 as well as CF_3 radicals in the decomposition of tris(trifluoromethyl)arsine. Further pyrolysis studies in the absence of glass, which probably reacts with arsenic trifluoride to give silicon tetrafluoride, would be of interest in view of the similar breakdown pattern observed in the mass spectrometer.

Experimental Section

The compounds were prepared by the literature methods[9-11] and their purity established by molecular weight determinations and infrared spectroscopy. Mass spectra were recorded on an A.E.I. MS9 operating at 70 ev, samples being introduced as vapor through a heated inlet at 185°. Perfluorotributylamine was added in some cases to assist in the counting of the spectrum.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, NORTH CAROLINA, AND THE SHIONOGI RESEARCH LABORATORY, SHIONOGI AND CO., LTD., FUKUSHIMA-KU, OSAKA, JAPAN

The Vibrational Spectrum of Borazine[1a]

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The vibrational spectrum of borazine, $(-BH-NH-)_3$, has been reexamined using isotopically labeled derivatives. On the basis of this study a revised assignment for a number of frequencies of the borazine spectrum is suggested. In particular, the two BN ring vibrations of species E′ have been identified at 1465 and 1406 cm^{-1} (gas phase spectrum), respectively.

Introduction

Borazine, $(-BH-NH-)_3$, the "inorganic benzene," has been known for more than 30 years, and its Raman and infrared spectrum was studied as early as 1939.[2] The basic assignments of the fundamental vibrations as suggested by Crawford and Edsall[2b] were refined by some later work[3] and have since been commonly accepted. Certain discrepancies between the observed and calculated values for out-of-plane hydrogen vibrations of the molecule were reinvestigated by Spurr and Chang,[4] and the assignments of BH and NH deformational modes of borazine are still somewhat controversial.[5] On the basis of their data Kubo and his coworkers[5] suggested that BH bending modes should occur at higher frequencies than the corresponding NH vibrations in each species. Nevertheless, the original assignments of the vibrational modes of borazine have generally been used in analyzing the spectra of substituted borazines. Only Becher[6] questioned the assignments of the B–N ring modes of species E′ of borazine, but no attempt was made to clarify that situation.

Recent studies of the vibrational spectra of other boron–nitrogen heterocycles containing the N–B–N entity raised some doubt about the validity of the original assignments for certain vibrational modes of borazine and have prompted a reexamination of the molecule. The findings of this study are substantiated through observations of isotopically labeled derivatives. The data resulting from isotope studies clarify several features of the vibrational spectrum of borazine which previously could not be resolved.

Due to multiple possibilities for labeling the borazine molecule, this compound is particularly suitable for a detailed study of isotope effects and a subsequent mathematical treatment. The results of such work based on the present experimental data will be reported elsewhere.

The authors gratefully acknowledge access to an unpublished manuscript on the vibrational spectra of B-trihaloborazines due to the courtesy of Professor J. Goubeau, Technische Hochschule Stuttgart, Germany.[7] This work arrives at conclusions similar to those arising from the present study with respect to the reassignment of the vibrational spectrum of borazine.

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