studies on d^4 systems currently being made in these laboratories.[22]

Acknowledgment.—The authors acknowledge the support of the National Science Foundation for this study. Discussions with Dr. A. D. Liehr and Professors K. Knox and D. Whitman are greatly appreciated.

(22) Originally it was thought that tetrahedral species may be producing the low-energy bands in manganese(III) complexes. However, data now available on $CrI_2 \cdot 2CH_3CN$ with excess I^- suggest this probably is not the case.

CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES,
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Vibrational Spectrum of the Hexafluorogermanate Ion

BY JAMES E. GRIFFITHS AND DONALD E. IRISH[1]

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The existence of the GeF_6^{2-} ion in acid solution has been demonstrated from an examination of the Raman effect. The three-line spectrum expected for a regular octahedral complex was observed, although slow secondary processes, presumably hydrolysis and HF–Pyrex glass interactions, were evident from the time dependent appearance of a number of other Raman lines. A complete vibrational analysis of the active fundamental modes of GeF_6^{2-} was possible by considering solid phase infrared spectra of NH_4^+, K^+, Rb^+, Cs^+, and Ba^{2+} hexafluorogermanates. In these, consideration of space group and site group selection rules was essential for a satisfactory interpretation of the observed spectra.

The most probable structure for an MX_6^{2-} (X = halogen) ion is a regular octahedron (O_h point group) or a slightly distorted octahedron (D_{4h} point group). In the latter, axial M–X bonds would be longer or possibly shorter than the equatorial ones. Especially in the case of the GeF_6^{-2} and $GeCl_6^{2-}$ ions, there is the possibility that the D_{4h} model might prevail over the more spherically symmetrical O_h model. It can be argued, for example, that diffuse vacant 4d orbitals would not contract sufficiently in the field of the fluorines or chlorines to form six equivalent sp^3d^2 orbitals.

The results of early X-ray diffraction work[2-4] on GeF_6^{2-} compounds suggested that subtle differences between axial and equatorial Ge–F bond lengths existed, but these could not be evaluated. On the other hand, conductance measurements[5] and other solution studies[6] do not unambiguously establish the existence of the GeF_6^{2-} species in solution. Accordingly, it seemed attractive to explore some of these problems using vibrational spectroscopic methods.

Experimental

Fluorogermanic acid solutions and the barium and cesium hexafluorogermanates were made by standard methods[4,7] and X-ray powder patterns agreed with published data. The ammonium salt was crystallized from an $NH_4F–H_2GeF_6$ solution at 85° rather than at lower temperatures with the expectation that the octahedral form would be formed in preference to the more usual hexagonal form.[2,8] The potassium and rubidium salts were from Sylvania Electric Products, Inc., Towanda, Pennsylvania, and were used as received.

Raman displacements from the 4358 Å. Hg line were obtained photoelectrically using a Cary Model 81 spectrophotometer. Although fresh fluorogermanic acid solutions, which had been prepared in polyethylene containers, seemed clear when they were first put in the glass Raman sample tubes, colloidal particles soon formed. This unavoidably resulted in high noise levels and a strong background intensity. The determination of depolarization factors, especially for the two weaker lines, was therefore precluded.

Infrared spectra from 2000 to 250 cm.$^{-1}$ were recorded with a Perkin-Elmer Model 421 spectrophotometer and samples were pressed in CsI disks. The absence of cleavage planes and the softness of cesium iodide made it difficult to reduce the particle size except by prolonged grinding with an agate mortar and pestle. The spectrum of $BaGeF_6$ was also recorded on a sample prepared as a Nujol mull pressed between polyethylene plates.

Results and Discussion

Selection Rules and Raman Spectra.—If the GeF_6^{2-} species belongs to the O_h point group, the irreducible representation of internal motion is

$$\Gamma = a_{1g}(R,p) + e_g(R,dp) + 2f_{1u}(IR) + f_{2g}(R,dp) + f_{2u}(\text{inactive})$$

whereas for D_{4h} symmetry[9]

$$\Gamma = 2a_{1g}(R,p) + 2a_{2u}(IR) + b_{1g}(R,dp) + b_{2g}(R,dp) + b_{2u}(\text{inactive}) + e_g(R,dp) + 3e_u(IR)$$

Raman results which appear in Table I and Fig. 1 show quite clearly that the most probable structure for the

TABLE I
RAMAN SPECTRUM OF THE GeF_6^{2-} ION

Frequency, cm.$^{-1}$	627	454	318
Assignments	ν_1 (a_{1g})	ν_2 (e_g)	ν_5 (f_{2g})

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(1) Summer visitor at Bell Telephone Laboratories, Inc., 1963.

(2) J. L. Hoard and W. B. Vincent, *J. Am. Chem. Soc.*, **61**, 2849 (1939).

(3) J. L. Hoard and W. B. Vincent, *ibid.*, **62**, 3126 (1940).

(4) R. W. G. Wykoff and J. H. Miller, *Am. J. Sci.*, **13**, 347 (1927).

(5) R. H. Schmitt, E. L. Grove, and R. D. Brown, *J. Am. Chem. Soc.*, **82**, 5292 (1960).

(6) R. L. Benoit and J. Place, *Can. J. Chem.*, **41**, 1170 (1963), and references cited therein.

(7) C. J. Hoffman and H. S. Gutowsky, *Inorg. Syn.*, **4**, 147 (1953).

(8) B. K. Vainshtein and R. K. Kurdyumova, *Kristallografiya*, **3**, 29 (1958).

(9) G. Herzberg, "Infrared and Raman Spectra," Vol. II, D. Van Nostrand Company, Inc., Princeton, N. J., 1945.

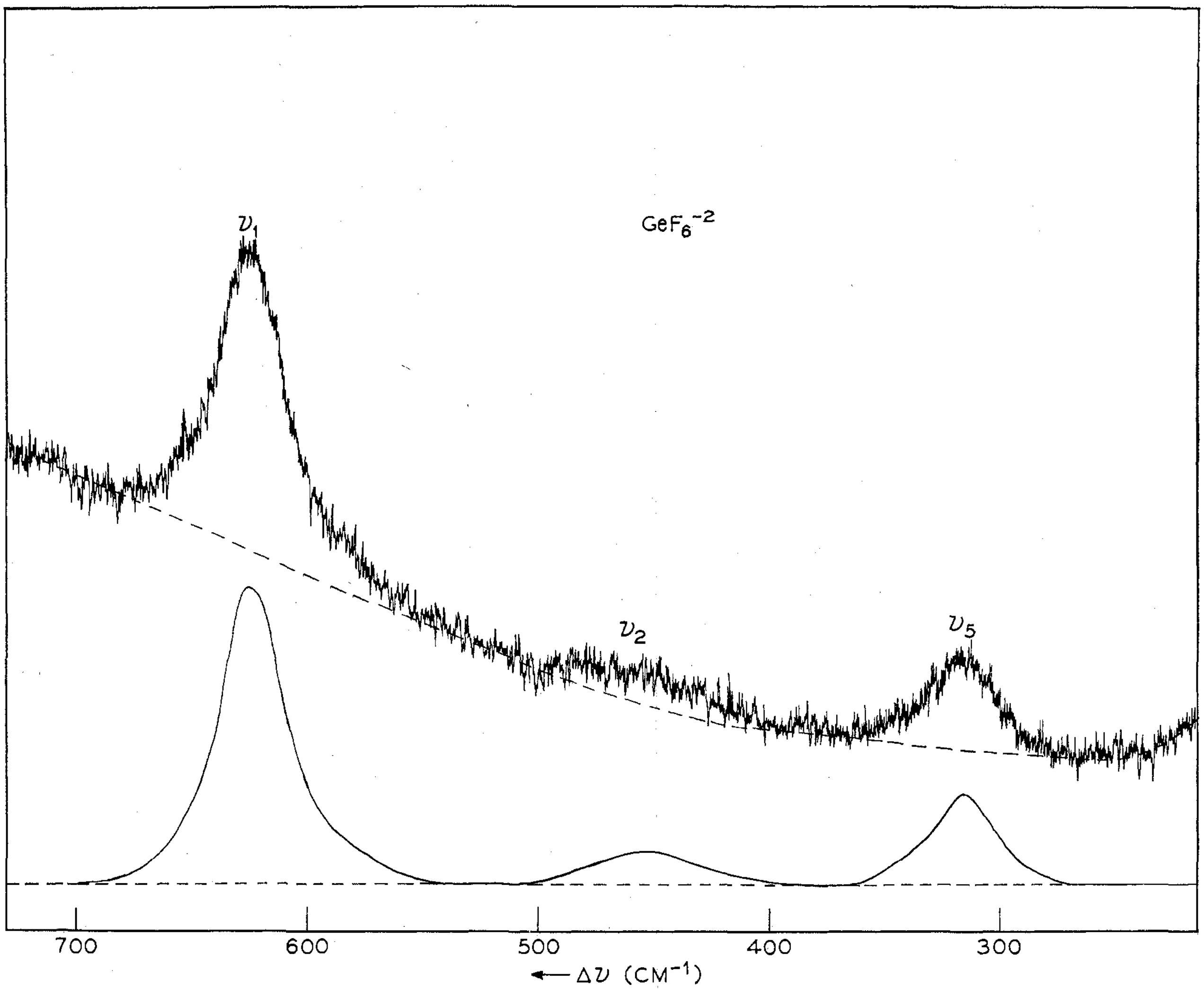

Fig. 1.—Raman spectrum of the GeF_6^{2-} ion. The upper trace is the observed spectrum and the lower trace represents the spectrum with background corrections applied.

GeF_6^{2-} ion is the regular octahedron. Although this is convincing evidence for the existence of the GeF_6^{2-} ion in acid solution, the slow growth of a large number of additional lines during 24 hr. indicates that hydrolysis or side reactions between HF and the glass sample tube or both are important. These secondary processes, although interesting, have not been studied further at this time.

Infrared Spectra.—In the infrared spectrum, only two bands are expected for the GeF_6^{2-} species provided other perturbations are absent or weak. Lengthening or shortening of one pair of *trans* Ge–F bonds, aside from the effect this would have on the frequencies of the fundamentals, would alter the point group from O_h to D_{4h} and should result in five infrared active bands. Observation of additional bands might therefore be interpreted as evidence for D_{4h} symmetry, as has recently been done for $BaSiF_6$.[10] Evidence of this sort is not convincing, however, for a five-band spectrum can be explained more realistically by considering the site symmetry of the ion under study. Halford[11] has discussed the selection rules for vibrational spectra of crystals when the space group and the number of molecules per unit cell are known. Space groups of the cesium, ammonium, and barium hexafluorogermanates and the site groups for the anions are listed in Table II.

TABLE II

STRUCTURAL DATA FOR THE HEXAFLUOROGERMANATES

Cation	Space group	Site group	Molecules per unit cell	Ref.
Cs^+	O^5_h	O_h	4	4
NH_4^+ (hex.)	D^3_{3d}	D_{3d}	1	2
(cubic)	O^5_h	O_h	4	8
Ba^{2+}	D^3_{3d}	D_{3d}	1	3

These particular salts were selected to show the effect of anion site symmetry on the observed spectra. The cesium salt should show only two bands whereas the barium salt should have five infrared bands.

$$\Gamma(D_{3d}) = 2a_{1g}(R,p) + a_{1u}(\text{inactive}) + 2a_{2u}(IR) + 2e_g(R,dp) + 3e_u(IR)$$

The spectrum of the ammonium salt is expected to have two or five infrared bands depending on which crystal modification is present.

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[10] I. R. Beattie, G. P. McQuillan, L. Rule, and M. Webster, *J. Chem. Soc.*, 1514 (1963).

[11] R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

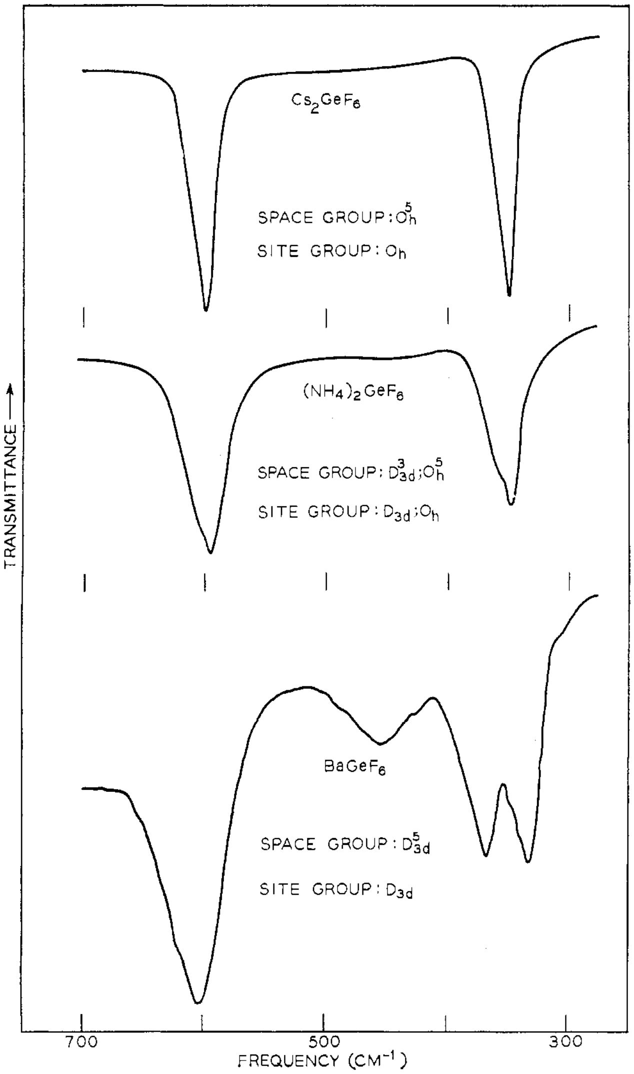

Fig. 2.—Infrared spectra of Cs_2GeF_6, $(NH_4)_2GeF_6$, and $BaGeF_6$ in CsI disks.

It is apparent from the results in Fig. 2 that site symmetry considerations correctly predict the observed spectra for the cesium and barium salts. The lowering of the symmetry of the anion in barium hexafluorogermanate does not result from Ge–F bond length alterations but rather from the position of the cation in the lattice. If the number of observed bands were due to elongation of a pair of Ge–F bonds, the infrared active antisymmetric F–Ge–F stretching mode (corresponding to the a_{2u} fundamental arising from the splitting of the degeneracy of the ν_3 mode, $f_{1u}(O_h) \rightarrow a_{2u} + e_u(D_{4h})$) should shift to a lower frequency. Specifically, one might expect the a_{2u} fundamental to occur at a lower frequency than the observed 602 cm.$^{-1}$ band reflecting the weaker F–Ge–F linkage in such an ion. In the absence of such a frequency shift, we may conclude that anion changes are not significant. Furthermore, it has been shown that the splitting of the degeneracy of the low frequency f_{1u} mode in the barium salt is not due to a double decomposition with the CsI pellet material by recording a spectrum of the sample in a Nujol mull. The splitting occurred here as well.

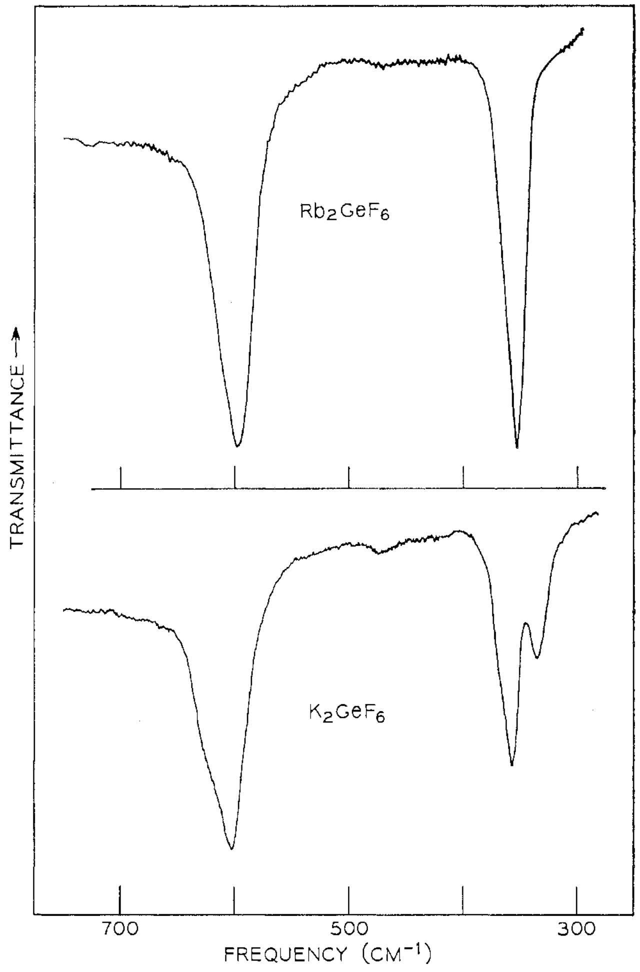

Fig. 3.—Infrared spectra of Rb_2GeF_6 and K_2GeF_6 in CsI disks.

The data for the ammonium salt does not allow an unambiguous choice between D_{3d} or O_h anion site symmetries. Although the latter is favored by the spectra and the method by which the salt was prepared, the suggestion of a shoulder on the low frequency band (Fig. 2) indicates that some of the hexagonal form may be present. The final choice of the predominant form requires more definitive evidence.

The spectra of K_2GeF_6 and Rb_2GeF_6 were also recorded (Fig. 3) because of the interesting structural features in their lattices. In the potassium salt, the cations have nine fluorine neighbors at 2.85 Å. and three at 3.01 Å.,[2] and therefore the degeneracies of the f_{1u} modes should be split, each giving two bands. The rubidium ions, however, are intermediate in size between potassium and cesium ions and, although the site group of the GeF_6^{2-} species in Rb_2GeF_6 is formally lower than O_h, each cation is surrounded by twelve practically equidistant fluorine atoms.[12,13] It was of interest to see if the trivial deviations from a regular O_h site group would be reflected in the infrared spectrum.

The spectrum of the potassium salt shows the splitting of the low frequency ν_4 (f_{1u}) fundamental band into two bands at 358 and 335 cm.$^{-1}$ but not in the case of the rubidium salt (ν_4 (f_{1u}) = 353 cm.$^{-1}$). The higher frequency band (ν_3 = 598 cm.$^{-1}$) is more nearly sym-

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(12) H. Bode and R. Brockmann, *Z. anorg. allgem. Chem.*, **269**, 173 (1952).

(13) W. B. Vincent and J. L. Hoard, *J. Am. Chem. Soc.*, **64**, 1233 (1942).

TABLE III

FUNDAMENTAL FREQUENCIES (CM.$^{-1}$) OF GeF_6^{2-}

No.	Species	Intensity	Activity	Assignment
1	a_{1g}	s	Raman	627
2	e_g	w	Raman	454
3	f_{1u}	s	Infrared	600
4	f_{1u}	s	Infrared	350
5	f_{2g}	m	Raman	318
6	f_{2u}	..	Inactive	...

metrical for Rb_2GeF_6 than for K_2GeF_6, where the appearance of a higher frequency contribution to the intensity indicates two bands at 602 and 635 cm.$^{-1}$. Moreover, a very weak band near 465 cm.$^{-1}$ in the spectrum of the potassium salt correlates with the similar band observed at 452 cm.$^{-1}$ in the spectrum of $BaGeF_6$.

On the basis of the above evidence, it would seem that additional bands, over that expected for a regular octahedral ion, indicate a lowered site symmetry. The opposite may not always be precisely true, however. It also follows that when additional bands are observed in the spectra of complex molecules which contain very symmetrical ions, the spectral complexities do not necessarily arise from structural changes in the ions but may only reflect changes in their site symmetries.

Assignments.—The observed Raman and infrared spectral data of fluorogermanic acid solutions and of solid Cs_2GeF_6 are useful for establishing the fundamental frequencies of the hexafluorogermanate ion. The Raman line at 627 cm.$^{-1}$ is the strongest in the spectrum and is therefore assigned to the totally symmetric a_{1g} stretching vibration. The weak and broad band centered at 454 cm.$^{-1}$ is assigned to ν_2 (e_g) because, in general, such a stretching vibration occurs at a higher frequency than the bending mode, ν_5, of the f_{2g} species.

TABLE IV

INFRARED SPECTRA OF $(NH_4)_2GeF_6$ AND $BaGeF_6$[a]

$(NH_4)_2GeF_6$ (O_h^5)			$BaGeF_6$ (D_{3d}^3)		
No.	Species	Assignment	No.	Species	Assignment
1	a_{1g}	...	1	a_{1g}	...
2	e_g	...	2	a_{1g}	...
3	f_{1u}	598	3	a_{1u}	Inactive
4	f_{1u}	349	4	a_{2u}	602
5	f_{2g}	...	5	a_{2u}	337
6	f_{2g}	Inactive	6	e_u	635
			7	e_u	452
			8	e_u	367
			9	e_g	...
			10	e_g	...

[a] Frequencies are given in cm.$^{-1}$.

By the same reasoning, the infrared active bands at 600 and 350 cm.$^{-1}$ are assigned to ν_3 and ν_4, respectively. The remaining fundamental, ν_6 (f_{2u}), is inactive. The assignments are summarized in Table III and the data and assignments for the ammonium and barium hexafluorogermanate salts are listed in Table IV. For the barium salt, e_u and a_{2u} fundamentals are assigned arbitrarily for we have no reasonable means of establishing which is which at this time. Individual data for K_2GeF_6 and Rb_2GeF_6 appear in the text but are not reproduced again in tabular form.

Acknowledgments.—We are grateful to Drs. G. E. Walrafen and L. H. Sharpe for the use of the Raman and infrared spectrophotometers. The generous gift of samples of K_2GeF_6 and Rb_2GeF_6 from Sylvania Electric Products, Inc., is gratefully acknowledged. We also wish to thank an anonymous referee for suggesting that infrared spectra of samples in Nujol mulls would eliminate or confirm the possibility of double decomposition occurring during the preparation of CsI pellets.

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Preparation and Crystal Data for Lanthanide and Actinide Triiodides[1]

BY L. B. ASPREY, T. K. KEENAN, AND F. H. KRUSE

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Lattice parameters and crystal structure types for twelve lanthanide triiodides (excepting only promethium and europium) have been determined. Similar data have been obtained for yttrium, americium, and plutonium triiodides. Two structure types occur in the lanthanide triiodides. The lighter members, LaI_3 through NdI_3, have orthorhombic symmetry ($PuBr_3$ type) while the heavier members of the series are hexagonal (BiI_3 type). An analogous transition is observed in the actinide series between PuI_3 and AmI_3, the former being orthorhombic and the latter hexagonal. Treatment of AmI_3 with hydrogen at elevated temperatures gave no evidence of a divalent compound of americium.

Introduction

Though most of the lanthanide and many actinide trifluorides, trichlorides, and tribromides have been prepared and identified, few investigations of the chemistry of the corresponding triiodides have been published. The triiodides of lanthanum, neodymium, uranium, neptunium, plutonium, and americium were reported to have an orthorhombic structure.[2] Druding

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) W. H. Zachariasen, *Acta Cryst.*, **1**, 265 (1948).