and F–As–F angle were revised to 1.708 Å and 98°. These revised parameters are very close to those found in the present investigation.

If one of the fluorine atoms in $AsF_3$ is replaced by the less electronegative methyl group, the F–As–F angle changes very little[46] (96.2 ± 0.2° in $AsF_3$, 96 ± 4° in $CH_3AsF_2$). Methyl substitution appreciably influences the lengths of adjacent As–F bonds, however, increasing them from 1.706 Å to approximately 1.74 Å. Such a change is expected on the basis of the primary rules of Gillespie's valence shell–electron repulsion model.[47] On the other hand, Gillespie introduced a subrule to account for structures of the group V trihalides, arguing in favor of appreciable double-bond character for the As–F and P–F bonds in order to rationalize the apparently anomalous experimental F–X–F bond angles of 102 and 104° for $AsF_3$ and $PF_3$, respectively. It is now clear that the bond angles of the two compounds are not anomalously large, but rather are the smallest in their respective series. Therefore, the Gillespie subrule loses some of its significance.

[46] L. J. Nugent and C. D. Cornwell, NBS Report 7099, March 1961; *J. Chem. Phys.*, **37**, 523 (1962).

[47] R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); *Angew. Chem.*, **79**, 885 (1967); *Angew. Chem., Intern. Ed. Engl.*, **6**, 819 (1967); *J. Am. Chem. Soc.*, **82**, 5978 (1960).

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MCMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

# The $Cl_2F^+$ and $Cl_3^+$ Cations

BY R. J. GILLESPIE AND M. J. MORTON

*Received September 18, 1969*

The Raman spectra of the 2:1 adducts of ClF with $AsF_5$ and $BF_3$ show that the cation has the asymmetric $ClClF^+$ structure and not the symmetric $ClFCl^+$ structure previously reported.[1] The $AsF_6^-$ salt of $Cl_3^+$ has been prepared from ClF, $Cl_2$, and $AsF_5$. Low-temperature Raman spectra show that $Cl_3^+$ has $C_{2v}$ symmetry, and simple valence force constants have been calculated.

In a recent paper[1] Christe and Sawodny showed that ClF forms 2:1 adducts with the Lewis acids $AsF_5$ and $BF_3$. Low-temperature infrared spectra showed that these are salts of $AsF_6^-$ and $BF_4^-$. Three frequencies common to both compounds of 586, 529, and 293 $cm^{-1}$ were assigned to the cation and it was concluded that the cation probably had the symmetric $ClFCl^+$ structure. We report now the low-temperature Raman spectra of these salts and the preparation of the $Cl_3^+AsF_6^-$ salt and its vibrational frequencies.

The bands observed in the Raman spectra of $Cl_2F^+AsF_6^-$ and $Cl_2F^+BF_4^-$ are given in Tables I and II, together with our assignments. These differ from the assignments of Christe and Sawodny as we observe a strong Raman band at 744 $cm^{-1}$ in both salts (Figure 1), which was not seen in the infrared spectra. This we assign to the Cl–F stretch in the unsymmetrical $ClClF^+$ cation. The intense Raman peaks at 516 and 540 $cm^{-1}$ in the $BF_4^-$ salt and 528 and 535 $cm^{-1}$ in the $AsF_6^-$ salt can be assigned to the Cl–Cl stretch.

In the $AsF_6^-$ salt Christe and Sawodny assigned infrared bands at 586 and 593 $cm^{-1}$ to $\nu_2$(asymmetric stretch) of $ClFCl^+$ and bands at 569 and 555 $cm^{-1}$ to the overtone of the bending mode of $Cl_2F^+$ at 293 $cm^{-1}$ whereas we assign the Raman bands at 563 and 581 $cm^{-1}$ to $\nu_2(E_g)$ of $AsF_6^-$. The splitting of the Raman band is attributed to the removal of the degeneracy in the solid state probably as a consequence of fluorine bridging. This also causes $\nu_2$ to be active in the infrared spectrum and accounts for two of the infrared peaks in the band in the region 555–593 $cm^{-1}$, the remaining two being assigned following Christe and Sawodny to the overtone of $\nu_3$(bend) of $ClClF^+$. Recently[2] we showed that in the salt $ClF_2^+AsF_6^-$ the Raman frequency of 544 $cm^{-1}$ (ir: 520 and 558

TABLE I

INFRARED AND RAMAN SPECTRA OF $Cl_2F^+AsF_6^-$

| Infrared,[a] $cm^{-1}$ | Raman, $\Delta\nu$, $cm^{-1}$ | Assignment $Cl_2F^+$ | Assignment $AsF_6^-$ |
|---|---|---|---|
| 258 mw | | | |
| 293 m | 293 (20)[b] | $\nu_3$ (bend) | |
| | 299 | | |
| | 375 (12) | | $\nu_5$ |
| 397 ms | | | $\nu_4$ |
| 514 vw, sh | | | |
| 520 vw | | | |
| 527 mw | 528 (100) | $\nu_2$ (Cl–Cl str) | |
| 535 m | 535 | | |
| 555 m | | $2\nu_3$ | $\nu_2$ |
| 569 vw | 563 (16) | | |
| 586 mw | 581 (12) | | |
| 593 m | | | |
| | 685 (70) | | $\nu_1$ |
| 703 vs | 744 (78) | $\nu_1$ (Cl–F str) | $\nu_3$ |

[a] Reference 1. [b] Figures in parentheses give the relative intensities (peak heights) of the observed Raman bands.

---

[1] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).

[2] R. J. Gillespie and M. J. Morton, *ibid.*, **9**, 616 (1970).

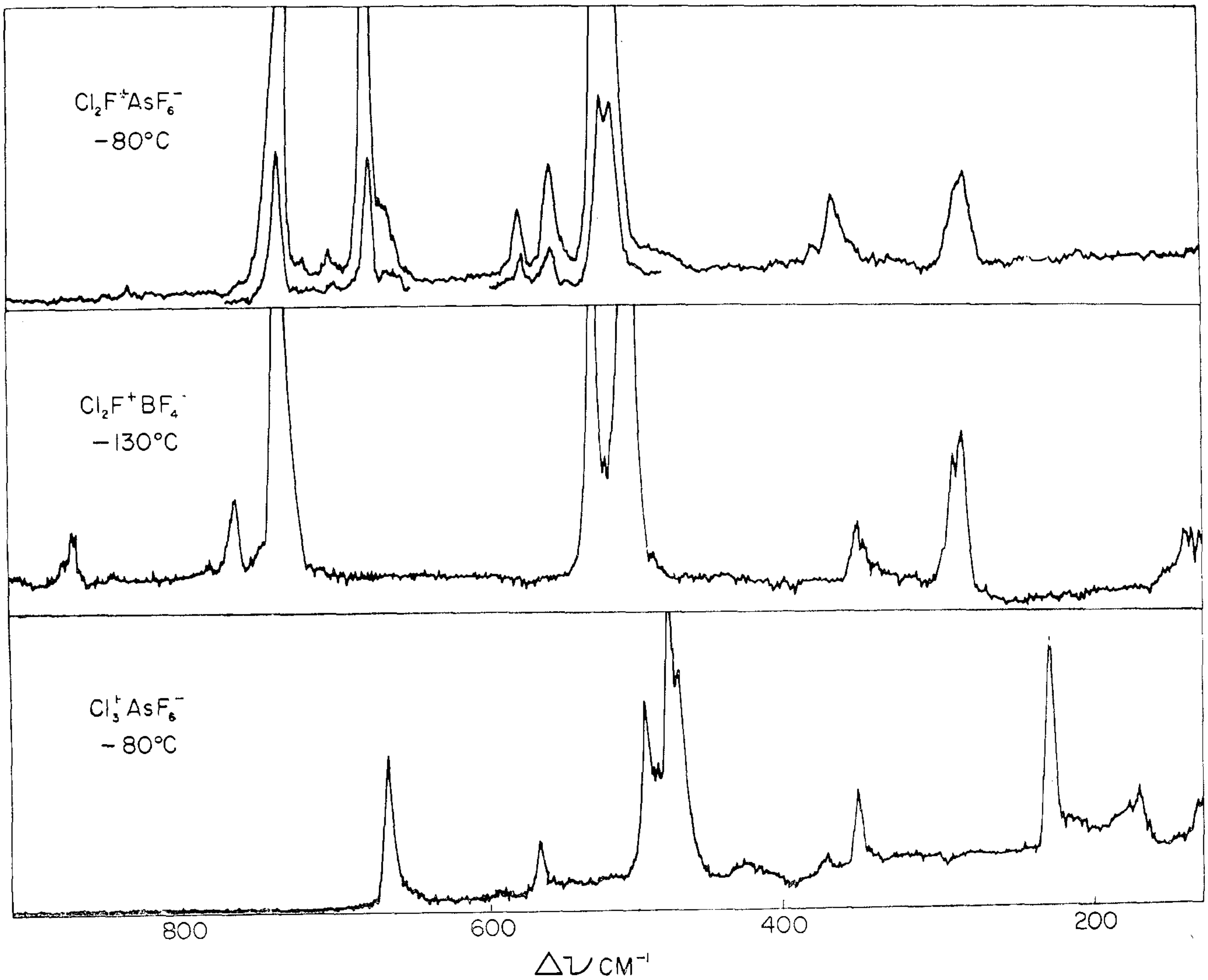


Figure 1.—Raman spectra for $Cl_2F^+AsF_6^-$, $Cl_2F^+BF_4^-$, and $Cl_3^-AsF_6^-$.

Table II

Infrared and Raman Spectra of $Cl_2F^+BF_4^-$

| Infrared, $cm^{-1}$ | Raman, $\Delta\nu$, $cm^{-1}$ | Assignment $Cl_2F^+$ | Assignment $BF_4^-$ |
|---|---|---|---|
| | 296 (35) | $\nu_3$ (bend) | |
| | 361 (10) | | $\nu_2$ |
| 511 w, sh | | | |
| 519 m | 516 (100) | $\nu_2$ (Cl–Cl str) | $\nu_4$ |
| 528 mw | | | |
| 532 mw, sh | 540 (90) | | |
| 572 mw | | | $B_2F_7^-$ |
| 588 w, sh | | $2\nu_3$ | |
| 594 m | | | |
| | 743 (90) | $\nu_1$ (Cl–F str) | |
| 770 mw | 771 (17) | | $\nu_1$ |
| | 874 (8) | | $B_2F_7^-$ |
| 950–1130 vs | 990 (4) | | $\nu_3$ |

$cm^{-1}$) had been assigned incorrectly to the bending mode of the cation.[3] We observed this bending mode at 384 $cm^{-1}$ and we assigned Raman bands at 544 and 602 $cm^{-1}$ to $\nu_2$ of $AsF_6^-$. Again the large splitting and the appearance of the band in the infrared spectrum was attributed to removal of the degeneracy which was attributed to strong fluorine bridging. Table III shows how the frequency $\nu_1$ of $AsF_6^-$ decreases and the splitting of $\nu_2$ decreases in the series $ClF_2^+AsF_6^-$, $Cl_2F^+AsF_6^-$, $Cl_3^+AsF_6^-$, in which it seems reasonable to suppose that the extent of fluorine bridging decreases as the cation becomes a poorer acceptor.

Table III

Variation of the Frequencies of $\nu_1$ and $\nu_2$ for the $AsF_6^-$ Ion with the Nature of the Cation

| | $AsF_6^-$[a] | $ClF_2^+AsF_6^-$ | $Cl_2F^+AsF_6^-$ | $Cl_3^+AsF_6^-$ |
|---|---|---|---|---|
| $\nu_1$ | 733 | 693 | 685 | 674 |
| $\nu_2$ | | 544 | 563 | 571 |
| | | 602 | 581 | |

[a] L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967).

In the $BF_4^-$ salt we again assign the band at 743 $cm^{-1}$ to the Cl–F stretch of the cation, and the strong bands at 516 and 540 to the Cl–Cl stretch probably split by factor group splitting. The additional weak Raman band at 874 $cm^{-1}$ and the weak infrared band at 572 $cm^{-1}$ may be due to the $B_2F_7^-$ anion which is stable at low temperatures.[4] The infrared bands at 588 and 594 $cm^{-1}$ assigned to $\nu_3$ of $FCl_2^+$ by Christe and Sawodny we assign to the overtone of the 296-$cm^{-1}$ bending frequency of $Cl_2F^+$.

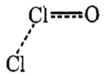
Christe and Sawodny pointed out[1] that the $FCl_2^+$

---

(3) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313 (1967).

(4) S. Brownstein, *Can. J. Chem.*, **45**, 2403 (1967).

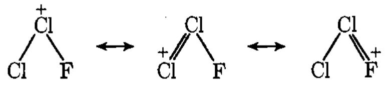
cation is isoelectronic with $OCl_2$. However the differences between the frequencies for this molecule ($\nu_3$ 686 $cm^{-1}$, $\nu_1$ 640 $cm^{-1}$, and $\nu_2$ 300 $cm^{-1}$) and those of 586, 529, and 293 $cm^{-1}$ that they attribute to the $FCl_2^+$ cation are considerably greater than is usual for simple isoelectronic molecules. The unsymmetrical $Cl_2F^+$ cation is, at least in a formal sense, isoelectronic with the molecule ClClO, which Rochkind and Pimentel[5] have shown to have stretching frequencies of 960 and 375 $cm^{-1}$. These authors estimated the frequency of the ClO molecule to be 970 ± 20 $cm^{-1}$ and concluded that the ClClO molecule was bent with a very weak Cl–Cl bond and a Cl–O stretching frequency little shifted from that of the diatomic molecule



However in the ClClF$^+$ cation the charge distribution may be expected to be markedly different with the positive charge spread over the chlorine atoms resulting in a stronger chlorine–chlorine bond and less double-bond character in the Cl–F bond than in the Cl–O bond. The observed frequencies are in agreement with this prediction, as the Cl–F frequency of 744 $cm^{-1}$ is not very different from that in ClF (785 $cm^{-1}$)[6] and the Cl–Cl frequency of 530 $cm^{-1}$ lies between that of chlorine[7] (558 $cm^{-1}$) and that of $\nu_1$ in $Cl_3^+$ (489 $cm^{-1}$).

In view of the complete lack of structural information on $Cl_2F^+$ it did not seem worthwhile to attempt any force constant calculations on the basis of the observed frequencies for the molecule, as even in a simple valence force field treatment there are five undetermined parameters and only three observed frequencies.

In justification of their symmetrical structure ClFCl$^+$ for the ion Christe and Sawodny stated that as F–Cl is polar with the negative charge concentrated on fluorine, this would be expected to attract any positive ion, in this particular case the Cl$^+$ cation, to give the symmetrical ClFCl$^+$ cation. However it does not follow that because F carries a negative charge in FCl while Cl has a positive charge that F will necessarily be a better electron-pair donor than Cl. The effect of the positive charge on Cl in reducing its donor strength is probably counterbalanced by the fact that this charge can be dispersed and stabilized by the formation of multiple bonds with the ligands. This type of charge dispersal by multiple-bond formation is not possible for F$^+$ because of the rigid adherence of fluorine to the octet rule. Thus the bonding in ClClF$^+$ can be reasonably well described in terms of the following resonance structures the contribution of III presumably being rather small



I II III

By treating $Cl_2F^+AsF_6^-$ with an excess of chlorine a yellow solid, stable only at low temperatures, was obtained. The Raman spectrum of this compound is given in Table IV. A very satisfactory assignment of the observed frequencies can be made on the basis that the compound is $Cl_3^+AsF_6^-$. The $Cl_3^+$ cation has not been previously reported although the $I_3^+$ and $Br_3^+$ cations are well established.[8,9] The spectrum shows the Raman-active frequencies of the $AsF_6^-$ ion together with three relatively intense bands at 490 (split to 485 and 493), 225, and 508 $cm^{-1}$. These we assign to $\nu_1$, $\nu_2$, and $\nu_3$, respectively, of the $Cl_3^+$ cation. No bands were observed above the band at 674 $cm^{-1}$ ($\nu_1$, $AsF_6^-$) indicating the absence of any Cl–F stretching modes. We note that the assigned frequencies are very close to the vibrational frequencies of the isoelectronic $SCl_2$ molecule[10] (514, 208, and 535 $cm^{-1}$), which has a bond angle of 103°, and we conclude that the $Cl_3^+$ cation has a similar structure. Using a simple valence force field, two frequencies and the bond angle are required to calculate the stretching force constant $f$ and the bending force constant $d$. These values can then be used to calculate $\nu_1$. The results of these calculations are given in Table V and give good agreement for a bond angle of 100° with force constants $f = 2.5$ mdyn Å$^{-1}$ and $d = 0.36$ mdyn Å$^{-1}$. In view of the qualitative nature of such calculations and the fact that our observed frequencies are for the solid state, we do not feel that a more elaborate treatment is justified.

TABLE IV

RAMAN SPECTRUM OF $Cl_3^+AsF_6^-$ (−80°)

| Rel intens (peak height) | Raman shift, $\Delta\nu$, $cm^{-1}$ | Assignment | |
|---|---|---|---|
| | | $Cl_3^+$ | $AsF_6^-$ |
| 20 | 170 | | |
| 75 | 225 | $\nu_2$ | |
| 25 | 370 | | $\nu_5$ |
| 6 | 394 | | $\nu_4$ |
| 75 | 485 | $\nu_1$ | |
| 100 | 493 | | |
| 60 | 508 | $\nu_3$ | |
| 18 | 571 | | $\nu_2$ |
| 50 | 674 | | $\nu_1$ |

TABLE V[a]

FORCE CONSTANTS FOR THE $Cl_3^+$ CATION IN $Cl_3^+AsF_6^-$

| | Angle, deg | | |
|---|---|---|---|
| | 95 | 100 | 105 |
| $f$, mdyn $cm^{-1}$ | 2.59 | 2.48 | 2.39 |
| $d$, mdyn $cm^{-1}$ | 0.369 | 0.356 | 0.342 |
| Calcd $\nu_1$, $cm^{-1}$ | 508 | 491 | 471 |

[a] $\nu_1$ 490 $cm^{-1}$, $\nu_2$ 225 $cm^{-1}$, and $\nu_3$ 508 $cm^{-1}$.

The stretching force constant of 2.5 mdyn Å$^{-1}$ is less than that in chlorine.[10] This is in contrast to the situation in $ClF_2^+$ for which the stretching force constant is larger than in $ClF_3$.[2,3] This probably indicates considerable double-bond character between

---

[5] M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.*, **46**, 4481 (1967).

[6] V. Gutmann, Ed., "Halogen Chemistry," Vol. I, Academic Press, London and New York, 1967.

[7] H. Stammreich and R. Forneris, *Spectrochim. Acta*, **17**, 775 (1961).

[8] R. J. Gillespie, R. A. Garrett, and J. B. Senior, *Inorg. Chem.*, **4**, 563 (1965).

[9] R. J. Gillespie and M. J. Morton, *Chem. Commun.*, 1565 (1968).

[10] H. Siebert, "Anwendung der Schwingungsspektroskopie in der Anorganischen Chemie," Spring-Verlag, Berlin, 1966.

the central chlorine and the fluorine in the $ClF_2^+$ cation which is not present in $Cl_3^+$.

We have not been able to obtain the spectrum of $ClClF^+$ in solution and it appears that it is completely disproportioned even at low temperatures according to $2ClClF^+ \rightarrow ClF_2^+ + Cl_3^+$. Thus in a solution of ClF in excess $SbF_5$ and HF at −76° in addition to the rather complicated spectrum attributable to $SbF_5$ and $SbF_6(SbF_5)_n^-$ the only other band observed was a strong, rather broad peak at 500 $cm^{-1}$ which can be assigned to $\nu_1$ of $Cl_3^+$. No lines that could be attributed to $ClClF^+$ were observed. Unfortunately the spectrum of $ClF_2^+$ was obscured by the solvent spectrum.

It seems reasonable to regard the cations $ClClF^+$ and $Cl_3^+$ as being derived from the coordination of $Cl^+$ with the ClF and $Cl_2$ molecules, respectively. Thus ClF can be displaced from $ClClF^+$ by chlorine to give the $Cl_3^+$ cation. Hence we expect to be able to prepare other cations such as $ClBrF^+$ and $ClBrBr^+$ by displacing the ClF in $ClClF^+$ with BrF or $Br_2$.

## Experimental Section

**Materials.**—All substances were handled in a Monel vacuum line fitted with Whitey valves with Kel-F seats, to which Kel-F traps were attached with Swagelok fittings. The line was well aged by treatment with $ClF_3$ and ClF. Chlorine monofluoride and antimony pentafluoride (Ozark-Mahoning Co.) and bromine trifluoride (Matheson Co., Inc.) were purified by several low-temperature vacuum distillations. Antimony pentafluoride was double-distilled at atmospheric pressure followed by vacuum distillation. Chlorine was bubbled through permanganate solution and concentrated sulfuric acid and distilled at −78°.

The compounds $Cl_2F^+AsF_6^-$ wand $Cl_2F^+BF_4^-$ were prepared exactly as described by Christe and Sawodny.[1] Samples were obtained in clear, thin-wall, 4-mm Kel-F tubes which were subsequently heat sealed under vacuum.

The compound $Cl_3^+AsF_6^-$ was prepared by warming $Cl_2F^+AsF_6^-$ in the presence of excess chlorine until all the solid had vaporized and then recooling to Dry Ice temperatures and pumping off the excess gases. Treatment of $Cl_2F^+AsF_6^-$ with $Cl_2$ in excess $AsF_5$ as solvent at −78° resulted in only partial conversion to $Cl_3^+AsF_6^-$ as the salts are not appreciably soluble in $AsF_5$.

$Cl_3^+AsF_6^-$ is a yellow solid completely dissociated to $Cl_2$, ClF, and $AsF_5$ at 25°. The intensity of the $AsF_5$ absorptions in a 10-cm Monel infrared cell fitted with silver chloride windows and Teflon gaskets had one-third of the intensity of the absorptions for pure $AsF_5$ at the same pressure.

**Raman Spectra.**—Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromator and a phototube detector with a dc electrometer amplifier and recorder. The 6328-Å exciting radiation was from a Spectra Physics Model 125 He–Ne laser giving approximately 30 mW at the sample.

The vertical laser beam was focused on the solids contained in a horizontal Kel-F tube mounted in a quartz tube with an evacuated jacket silvered except at the center. Nitrogen was boiled off from a dewar and passed through the quartz tube and the temperature was recorded with a thermocouple. Light scattered at 90° from the sample was focused on the slits of the monochromator so that the image of the Kel-F tube walls fell well outside the limits of the slit.

**Acknowledgment.**—We thank the National Research Council of Canada for financial support of this work and the Department of University Affairs, Province of Ontario, for the award of an Ontario Graduate Fellowship to M. J. M.

---

CONTRIBUTION FROM THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE RADIATION LABORATORY AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

# Sulfur Hexafluoride. Its Reaction with Ammoniated Electrons and Its Use as a Matrix for Isolated Gold, Silver, and Copper Atoms

BY LEO BREWER, CHIN-AN CHANG, AND BALDWIN KING

*Received September 24, 1969*

The reactivity of $SF_6$ with reactive metals was studied to explore the use of $SF_6$ as a matrix material for low-temperature isolation of metallic atoms. At 212°K $SF_6$ rapidly decolorized the blue liquid ammonia solutions of alkali metals to produce white precipitates of alkali fluorides and sulfides. The codeposition of Au vapor with $SF_6$ at 20°K gave well-isolated matrices with very sharp atomic spectra comparable to those obtained with inert-gas matrices, but Cu and Ag spectra in $SF_6$ were very broad. *n*-Perfluoroheptane was also examined as a matrix material, but Ag and Au gave very complex spectra.

## Introduction

The rare gases, which have been widely used[1] for matrix isolation of reactive species, are restricted to very low temperatures because of their low melting points. $SF_6$ with a melting point of 218°K is an attractive nonpolar molecule for matrix studies that could be extended to above liquid nitrogen temperatures. It is known to be chemically inert toward aqueous or fused alkali, ammonia, and oxygen and does not react appreciably with sodium metal[2] below 200° or with $CF_3$ or $CH_3$ radicals[3] up to 365°. The high electron affinity[4] and

---

(1) B. Meyer in "Low Temperature Spectroscopy; Optical Properties of Molecules in Matrices, Mixed Crystals, and Organic Glasses," Elsevier, Publishing Co., New York, N.Y., 1970, Chapter 9.

(2) H. C. Cowan, F. Reding, and E. Warhurst, *J. Chem. Soc.*, 4168 (1953).

(3) H. F. Le Fevre, J. D. Kale, and R. B. Timmons, *J. Phys. Chem.*, **73**, 1614 (1969).

(4) W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).