

INFRARED SPECTRA OF MATRIX-ISOLATED SPECIES IN THE GALLIUM-FLUORINE SYSTEM

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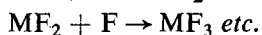
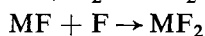
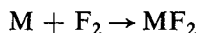
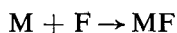
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SUMMARY

The species GaF₃, GaF, AlF₃, AlF and (AlF)₂ have been isolated in inert-gas matrices and their infrared absorption spectra obtained over the range 33–4000 cm⁻¹. The following techniques were used to generate these species; (i) co-deposition of Ga or GaF and molecular F₂ or F atoms with an excess of inert gas; (ii) Knudsen cell effusion and matrix isolation of the vapors over GaF₃, GaF₃ + Ga and GaF₃ + Al.

INTRODUCTION

Recently, many reduced-valency metal fluoride species have been synthesized by high-temperature techniques and characterized spectroscopically¹. The starting materials have usually been the most common form of the metal fluoride and the reduced-valency species were produced by superheating the vapor in the presence of an excess of the metal. For example, TiF₂ was produced *via* TiF₃(g) + Ti(s), ZrF₂ *via* ZrF₄(g) + Zr(s), SiF₂ *via* SiF₄(g) + Si(s), GeF₂ *via* GeF₄(g) + Ge(s), VF₂ *via* VF₃(g) + V(s) and AlF *via* AlF₃(g) + Al(s). However, this approach is thermodynamically less favorable for the production of species such as AlF₂, TiF, SiF and SiF₃. A more attractive synthesis route would be one of direct combination of the elements with rapid quenching and isolation of the products. Thus ideally one could expect, by controlling the stoichiometry and pressure of the co-reactants, to produce species with the desired valency; for example:



As a test of this technique, we have chosen the gallium + fluorine system. Under equilibrium conditions, one can expect to obtain GaF and GaF₃ which should provide an independent check on the identity of species produced with the presumably non-equilibrium co-condensation procedure.

EXPERIMENTAL

The apparatus and general matrix-isolation techniques used are similar to those described elsewhere¹⁻³. Beckman IR-9 and IR-11 spectrometers* were used to cover the spectral regions 400–4000 cm⁻¹ and 33–600 cm⁻¹ respectively.

Effusion studies were carried out using graphite Knudsen cells and single- or double-cell techniques as described elsewhere³. Pure GaF₃ vaporizations were carried out over the temperature range 700–800°, *i.e.*, at cell pressures of *ca.* 10⁻⁵–10⁻⁴ atm. The F₂ reaction experiments were achieved by pre-mixing the F₂ with the matrix gas prior to deposition. No corrosion of the Cu trapping surface resulted from these experiments.

RESULTS AND DISCUSSION

Infrared spectra from GaF₃ vaporization

Very little is known about the spectra or identity of the molecular species over solid GaF₃. One expects, by analogy with other Group III halide studies⁴, that the predominant vapor species should be GaF₃ with relatively little contribution from polymeric or reduced species. There is also no reason to expect a GaF₃ molecule to be anything other than a *D*_{3h} symmetry species. The infrared spectra should therefore contain three absorptions, arising from the antisymmetric stretch ν_3 frequency and the in-plane ν_4 and out-of-plane ν_2 deformations. From the known spectra of AlF₃, we expect ν_3 to appear in the normal infrared region and ν_2 and ν_4 in the far-infrared.

Matrix-isolation infrared spectra for the region 400–4000 cm⁻¹ showed a strong absorption at 748.0 cm⁻¹ and 759.2 cm⁻¹ for argon and neon matrices respectively, which is assigned as ν_3 for GaF₃. Each of these absorptions could be resolved to yield the correct fine structure for the naturally occurring isotopic species ⁶⁹GaF₃ and ⁷¹GaF₃. With heavier matrix deposits, many relatively low-intensity absorptions were observed, as shown for example in Figure 1. An absorption in the regions of 610 cm⁻¹ and 590 cm⁻¹ for neon and argon matrices respectively (see Fig. 1) showed the appropriate isotopic structure for the GaF species, and in addition the frequency is in good general agreement with the

* Certain commercial equipment is identified in order to adequately specify the experimental procedure. Such identification does not imply endorsement by the National Bureau of Standards nor does it imply that the equipment is necessarily the best available for the purpose.

known gas-phase value⁵ of 615.8 cm^{-1} . Analogous spectra were obtained for N_2 and Kr matrices. The remaining low-intensity absorptions observed can be attributed to polymeric species such as $(\text{GaF}_3)_2$ and $(\text{GaF})_2$.

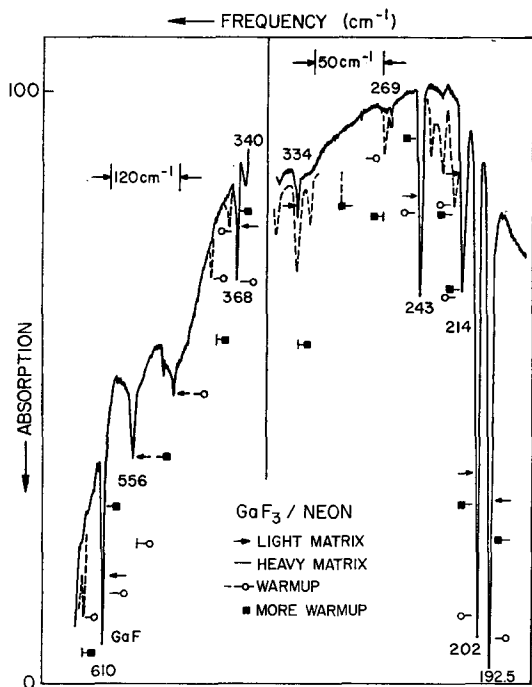


Fig. 1. Infrared spectra of GaF_3 in a Ne matrix. The labels indicate the absorption amplitudes at various conditions.

In the far-infrared region of $33\text{--}400\text{ cm}^{-1}$, relatively intense absorptions were observed in the vicinity of 202, 193, 187 and 212 cm^{-1} with Ne, Ar, Kr and N_2 matrices respectively. As indicated in Figure 1, these principal absorptions have a multiplet fine structure which might be attributed to the frequently observed matrix-splitting phenomenon. However, these multiplet features each show essentially the same decrease in intensity during matrix-warming experiments as did the ν_3 (GaF_3) absorptions and are therefore assigned as the ν_2 and ν_4 fundamental frequencies for GaF_3 . A relatively broad absorption in Kr matrices at 187 cm^{-1} most likely results from an overlap of ν_2 and ν_4 . In N_2 matrices, the ν_2 and ν_4 were separated by a wider frequency interval and each region was extensively split.

In view of the complexity of these spectra, we suggest that for the purpose of calculating vibrational partition functions for GaF_3 one should assume that ν_4 and ν_2 have approximately the same frequency which, in the gas phase, is estimated to fall in the range of $190 \pm 20\text{ cm}^{-1}$. It should be noted that a similar assignment has been given⁴ to the spectra of matrix-isolated AlF_3 .

The 243 cm^{-1} absorption occurred rather sporadically and was more sensitive to matrix warming than the features assigned to GaF and GaF₃. We believe that this is caused by the presence of an impurity.

Infrared spectra for GaF₃ vaporization under reducing conditions

Superheated GaF₃

Use of double-cell techniques, similar to those described elsewhere³, provides an effective means of reducing the possible presence of polymeric species such as (GaF₃)₂ or (GaF)₂ in the effusing vapor.

Typical spectra of superheated GaF₃ vapor are given in Figure 2 where it is apparent that the bands believed to be due to polymeric species are still present. Hence it is concluded that the observed aggregation results during the trapping process rather than in the Knudsen cell system.

The superheating procedure also produced an increased amount of the reduced species GaF. Complete reduction of GaF₃ to GaF was obtained by passing GaF₃ from a relatively cool cell ($\sim 750^\circ$) into a hot cell ($\sim 1020^\circ$) containing Ga metal.

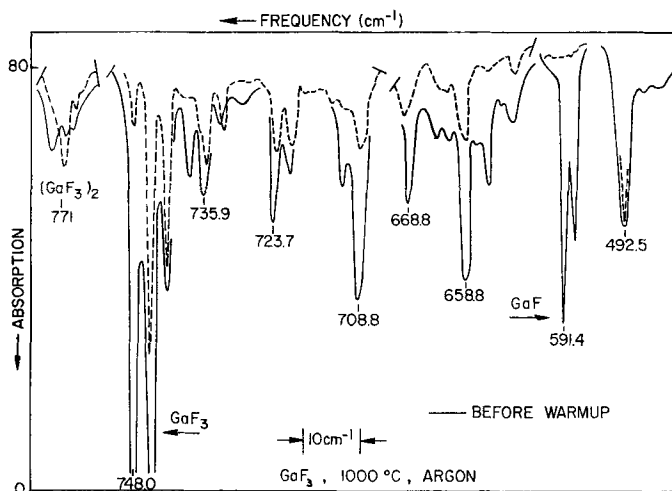


Fig. 2. Infrared spectra of superheated GaF₃ in an Ar matrix.

Al + GaF₃ system

Since AlF and AlF₃ are relatively more stable than the analogous gallium species, one might reasonably expect the reaction of GaF₃ with Al (especially under superheating conditions) to result in the formation of the mainly reduced gallium fluoride species. GaF₃ was passed from a relatively cool cell at 770° into a hot cell ($\sim 1000^\circ$) containing Al metal. The argon-matrix absorption spectra for the species AlF₃, AlF and (AlF)₂ have been reported previously⁴ and these species

are the major products in the present study. Notably no GaF_3 is present and only a small amount of GaF . Weak bands at 724 and 648 cm^{-1} were also present but remain unidentified.

Ga + F₂ system

Under equilibrium conditions, the predominant primary products of a $\text{Ga} + \text{F}_2$ reaction can be shown by thermodynamic calculations to be GaF and GaF_3 . It was hoped that co-condensation of a Ga molecular beam with F_2 and an excess of rare gas would result in the formation and isolation of kinetically, rather than thermodynamically, favored products such as $(\text{GaF}_2)_n$ where $n = 1$ or 2 . Typical results of this procedure are given by the spectra depicted in Figure 3. For a low concentration of F_2 relative to Ga atoms, GaF is indicated as the major product. The 547 cm^{-1} absorption of Figure 3 is attributed to $(\text{GaF})_2$ and the 748 cm^{-1} feature to GaF_3 . The 633 cm^{-1} and 664 cm^{-1} peaks remained unassigned and were not very reproducible. However, they did increase with an increasing Ga/F_2 ratio, and conceivably could result from the presence of GaF_2 . With a higher relative concentration of F_2 , GaF_3 was a predominant product in addition to GaF and $(\text{GaF})_2$. These results strongly suggest that the initial reaction of a gallium atom and a fluorine molecule produces GaF and a fluorine atom rather than GaF_2 . The fluorine atoms produced could however diffuse to the site of other GaF molecules and react to form a small amount of GaF_2 .

The presence of Ga_2F_2 is interesting since it could result from a direct reaction of Ga_2 and F_2 rather than from dimerization of GaF . The fact that the

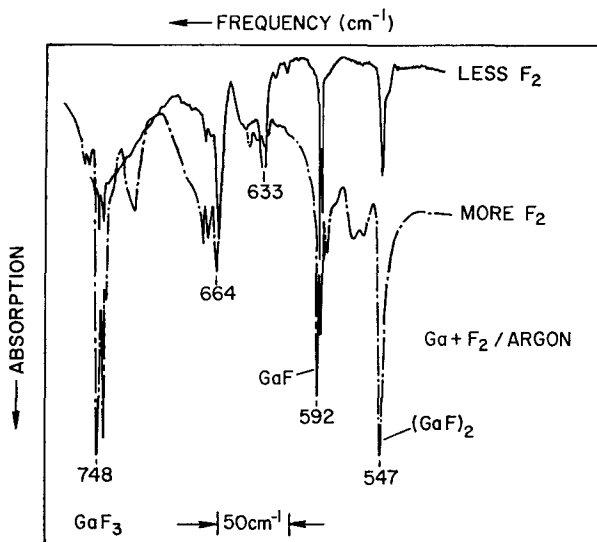


Fig. 3. Infrared spectra of species produced by co-condensation of a Ga molecular beam with F_2/Ar mixtures.

547 cm^{-1} band is of the same order in intensity as the monofluoride bands does suggest that it is formed from direct reaction of gallium and fluorine rather than through the formation of GaF.

GaF + F₂ photolysis system

In an effort to further promote the possible formation of GaF₂, the following reaction was carried out. A beam of GaF was generated by passing GaF₃ into a hot cell containing Ga metal. This was co-condensed with the F₂/Ar mixture. During trapping, the surface was irradiated with UV light from a quartz-jacketed Hg lamp. This procedure should have resulted in the formation of F atoms for reaction with GaF to produce GaF₂. However, no significant bands other than GaF and GaF₃ were noted even after prolonged photolysis.

CONCLUSIONS

The principal absorption frequencies assigned to gallium fluoride species are summarized in Table 1. One must conclude that the (GaF₂)_n species are considerably less stable than either GaF or GaF₃ and cannot be produced very effectively by the thermochemical or even the co-condensation reaction procedure. However, the ability to produce a reaction by merely co-condensing reactant beams of metal and F₂ is significant in that it may allow one to produce species that are difficult to generate by thermochemical techniques.

TABLE 1

INFRARED ABSORPTION FREQUENCIES IN THE GALLIUM-FLUORINE SYSTEM

Frequency (cm^{-1})	Matrix	Assignment	
745.0	Ar	⁷¹ GaF ₃	} ν_3
748.0	Ar	⁶⁹ GaF ₃	
756.2	Ne	⁷¹ GaF ₃	
759.2	Ne	⁶⁹ GaF ₃	
202	Ne	} GaF ₃	} ν_2 and ν_4
192	Ne		
193	Ar		
188	Ar		
187	Kr		
212	N ₂		
171	N ₂		
589.6	Ar	⁷¹ GaF	
591.5	Ar	⁶⁹ GaF	
607.1	Ne	⁷¹ GaF	
609.0	Ne	⁶⁹ GaF	

(continued)

TABLE 1 (continued)

Frequency (cm ⁻¹)	Matrix	Assignment
591	Kr	GaF
585	N ₂	GaF
575	Ar	(GaF) ₂
547	Ar	
416	Ar	
648.1	Ar	
724	Ar	

ACKNOWLEDGEMENTS

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REFERENCES

- 1 J. W. HASTIE, R. H. HAUGE AND J. L. MARGRAVE, in J. R. FERRARO AND S. RAO (Eds.), *Spectroscopy in Inorganic Chemistry*, Academic Press, New York, 1970, p. 57.
- 2 J. W. HASTIE, R. H. HAUGE AND J. L. MARGRAVE, *High Temp. Sci.*, 1 (1969) 76.
- 3 J. W. HASTIE, R. H. HAUGE AND J. L. MARGRAVE, *J. Chem. Phys.*, 51 (1969) 2648.
- 4 A. SNELSON, *J. Phys. Chem.*, 71 (1967) 3202.
- 5 R. F. BARROW, P. G. DODSWORTH AND P. B. ZEEMAN, *Proc. Phys. Soc.*, A70 (1957) 34.