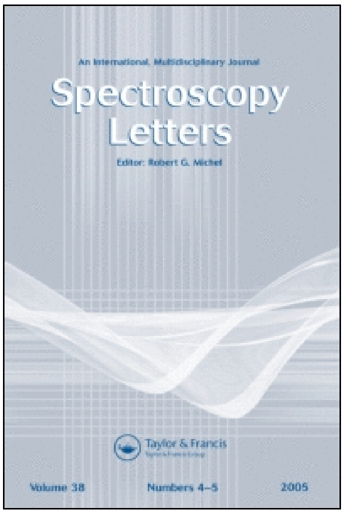
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Study of the Raman and Broadline NMR Spectra of $(GeF_2)_3\ GeF_4$

J. L. Margrave[a]; P. W. Wilson[a]; H. J. Hurst[b]
[a] Dept. of Chemistry, Rice University, Houston, Texas, U.S.A. [b] Chemical Technology Division Australian Atomic Energy Research Establishment Lucas, Heights, N.S.W., Australia

To cite this Article Margrave, J. L. , Wilson, P. W. and Hurst, H. J.(1973) 'A Study of the Raman and Broadline NMR Spectra of $(GeF_2)_3$ GeF_4', Spectroscopy Letters, 6: 3, 191 — 195
To link to this Article: DOI: 10.1080/00387017308065447
URL: http://dx.doi.org/10.1080/00387017308065447

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 6(3), 191-195 (1973)

A STUDY OF THE RAMAN AND BROADLINE NMR SPECTRA OF $(GeF_2)_3\ GeF_4$

J. L. Margrave and P. W. Wilson

Dept. of Chemistry, Rice University,
Houston, Texas, U.S.A.

and

H. J. Hurst

Chemical Technology Division
Australian Atomic Energy Research Establishment
Lucas Heights, N.S.W., Australia

Downloaded At: 04:30 30 January 2011

INTRODUCTION

The compound $(GeF_2)_3\ GeF_4$ has only recently been characterized[1]. A number of the physical and chemical properties of $(GeF_2)_3\ GeF_4$ are now known, including among others, its thermal behaviour and enthalpy of formation. The Raman spectrum and broadline NMR spectrum have not been presented and in this report they are described for the first time.

EXPERIMENTAL

$(GeF_2)_3\ GeF_4$ was prepared as described previously[1]. Briefly, Ge was heated to 350°C in the presence of one atmosphere pressure of GeF_4. A white compound formed on the cool parts of the apparatus and this has been shown to be $(GeF_2)_3\ GeF_4$. The compound is hygroscopic and all manipulations were performed in a dry box.

To obtain the Raman spectrum the compound was packed into a 2 mm glass tube. The actual spectrum was taken by the Spex Industries Laboratory service.

Copyright © 1973 by Marcel Dekker, Inc. All Rights Reserved. Neither this work nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Derivative spectra of the ^{19}F absorption signal at room temperature were obtained using a JEOL JNM-W-40 broadline spectrometer. Twenty g of sample was packed into a 15 mm diameter glass tube, and the spectrum was taken in the normal way.

RESULTS AND DISCUSSION

The Raman spectrum of $(GeF_2)_3$ is shown in Figure 1.

The assignment of the laser-Raman frequencies of $(GeF_2)_3$ GeF_4 is difficult and should be based on an understanding of its crystal structure and on the observed vibrational frequencies of other germanium fluorides.

Unfortunately the crystal structure of $(GeF_2)_3$ GeF_4 is not known nor is it presently possible to prepare it in a crystalline form and so

Downloaded At: 04:30 30 January 2011

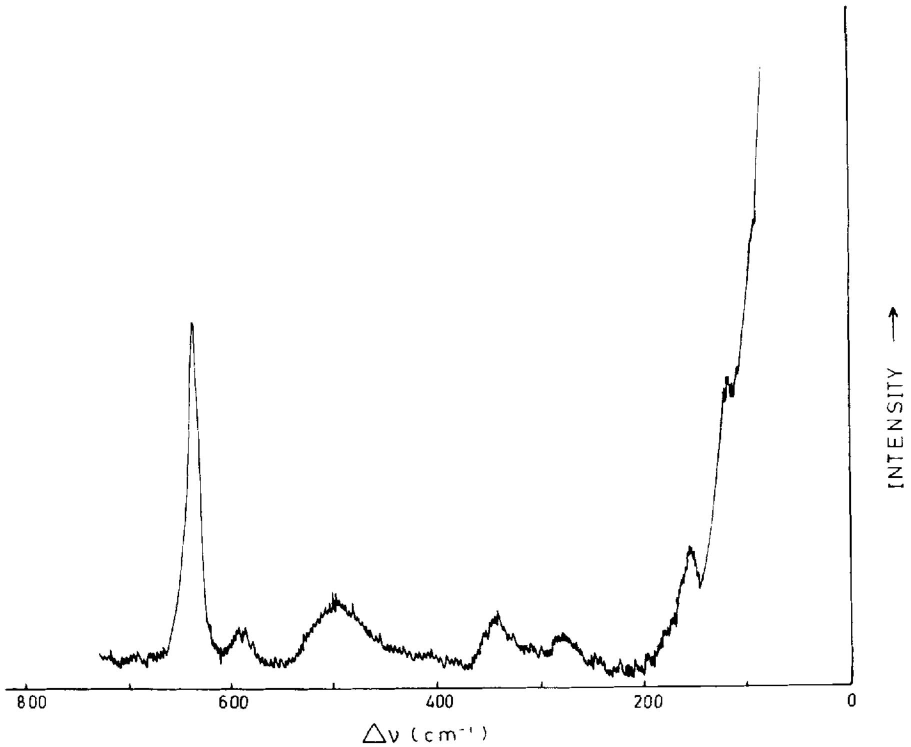


FIG 1.

Raman Spectrum of $(GeF_2)_3$ GeF_4

determine its structure. However the crystal structure of the closely related compound $(GeF_2)_4$ GeF_4 has recently been determined.[2] The space group of $(GeF_2)_4$ GeF_4 is no. 14 : $P_{21}/a(C^5_{2h})$. The structure comprises a three dimensional covalent lattice of octahedral GeF_6 groups and distorted square pyramidal GeF_4 groups. These units are held together by two types of fluorine bridging bonds. The geometry of the GeF_4 group is very similar to that observed in the compound GeF_2. One of the two types of linking -Ge-F-Ge-F- chains is common to both $(GeF_2)_4$ GeF_4 and GeF_2. It is not unreasonable to suggest that the crystal structure of $(GeF_2)_3$ GeF_4 should be very similar to that of $(GeF_2)_4$ GeF_4. In particular, the units from which the crystal lattice of $(GeF_2)_3$ GeF_4 is built will almost certainly be very similar to those encountered in $(GeF_2)_4$ GeF_4. An understanding of the Raman spectrum of $(GeF_2)_3$ GeF_4 can therefore be partially based on a knowledge of the crystal structure of $(GeF_2)_4$ GeF_4. It should be noted that a sufficient quantity of $(GeF_2)_4$ GeF_4 to determine its Raman spectrum cannot be isolated at the present time.

The vibrational frequencies of the hexafluorogermanate ion, GeF_6^{2-}, have been measured using Raman studies of solutions[3], and infra-red studies of pressed CsI discs and Nujol mulls[3]. The assignments agree with those predicted for O_h symmetry.

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	
	A_{1g}	E_g	T_{1u}	T_{1u}	T_{2g}	T_{2u}	
R	627 s	454 w	-	-	318 m	-	cm^{-1}
IR	-	-	600	350	-	-	cm^{-1}

While the three fundamental frequencies of gaseous GeF_2 molecules have been determined,[4,5]

ν_1	ν_2	ν_3	
692	263	663	cm^{-1}

Downloaded At: 04:30 30 January 2011

and matrix isolated GeF_2 shows sharp peaks in the region of 655 cm^{-1}, crystalline GeF_2 has no such sharp features[4]. The Raman spectrum of crystalline GeF_2[6] shows only a broad peak centered at 500 cm^{-1}. The distorted square pyramidal GeF_4 unit in this compound and in $(GeF_2)_3$ GeF_4 does not have a high degree of symmetry.

The most prominent feature in the Raman spectrum of $(GeF_2)_3$ GeF_4 is a strong line at 640 cm^{-1}. Such strong lines are usually associated with the totally symmetric stretching frequencies of groups with a centre of inversion. Although the GeF_6 groups of O_h symmetry in $(GeF_2)_4$ GeF_4 occupy sites with the much lower C_i symmetry, the Raman active frequencies A_{1g}, E_g, T_{2g} will continue to be Raman active, despite any splitting through perturbation, because the inversion centre is preserved. Assuming the GeF_6 group occupies a similar site in $(GeF_2)_3$ GeF_4, the strong line at 640 cm^{-1} could be associated with the A_{1g} symmetric stretch frequency. This corresponds to the strong line at 627 cm^{-1} observed for the hexafluorogermanate ion in solution. Weaker lines at 290 cm^{-1} and 470 cm^{-1} are in approximate agreement with the frequencies of T_{2g} and E_g symmetry. The broad band at 500 cm^{-1} seen in the Raman spectrum of crystalline GeF_2 is also present[6].

The results of the broadline NMR study were not as clear as the Raman spectrum study. The spectrum contained a broad and a narrow component, indicating two types of fluorine atoms. Their relative proportions could not however be determined because of uncertainties in different modulation broadening of the two components and in deconvolution of the integrated signal.

From the above discussion, it is clear that the Raman and broadline NMR spectra of $(GeF_2)_3$ GeF_4 are consistent with those that might be expected from a consideration of the crystalline habit of the molecule. This

Downloaded At: 04:30 30 January 2011

interpretation shows that the spectra are a composite of the contributions from the GeF_6 and GeF_4 group within the crystal. From other work it is reasonable to expect that other members of the family $(GeF_2)_x$ GeF_4 will be prepared[1,2]. Since it is likely that all members of this family will contain similar groupings in their crystalline habit, the preceding discussions may well be applicable to all members of the family.

REFERENCES

1. G.P. Adams, J.L. Margrave and P.W. Wilson, J. Inorg. Nucl. Chem., 33, 1301 (1971).
2. J.C. Taylor and P.W. Wilson, J. Am. Chem. Soc., in press.
3. J.E. Griffiths and D.E. Irish, Inorg. Chem., 3, 1134 (1964).
4. J.W. Hastie, R. Hauge and J.L. Margrave, J. Phys. Chem., 72 4492 (1968).
5. R. Hauge, V.M. Khanna and J.L. Margrave, J. Mol. Spectrosc., 27, 143 (1968).
6. J.L. Margrave and P.W. Wilson, Europ. Polym. J., 7, 1989 (1971).

Received January 15, 1973
Accepted January 31, 1973

Downloaded At: 04:30 30 January 2011