Submitted to
J. of Molecular Spectroscopy

LBL-1888
Preprint

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August 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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THE RAMAN SPECTRA OF SOLID XENON TETRAFLUORIDE AND ITS ADDUCT WITH XENON DIFLUORIDE

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ABSTRACT

The Raman spectra of the solids XeF_4 and $XeF_2 \cdot XeF_4$ show effects arising in intermolecular vibrational coupling. Assignments based on factor group analysis are proposed.

INTRODUCTION

The Raman[1] and infrared[2] spectra of gaseous xenon tetrafluoride have previously and properly been interpreted in terms of a XeF_4 molecule of D_{4h} symmetry, which has the vibrational representation $A_{1g} + B_{1g} + A_{2u} + B_{2g} + 2E_u$. For solid xenon tetrafluoride, Claassen *et al.*[2] observed only three Raman lines, which they assigned to fundamentals in the three Raman-active, *gerade* modes of a D_{4h} XeF_4 species: 543 cm^{-1}, ν_1 (A_{1g}); 502 cm^{-1}, ν_4 (B_{2g}); 235 cm^{-1}, ν_3 (B_{1g}).

During recent investigations made in this laboratory of complex formation between xenon tetrafluoride and antimony pentafluoride[3-5], the purity of the xenon tetrafluoride used was routinely checked by recording the Raman spectra of the solid. The discrepancy observed between our Raman spectra and those previously published prompted the detailed investigation and analysis of the Raman spectrum of solid xenon tetrafluoride described in this paper; included are data for the crystalline adduct $XeF_2 \cdot XeF_4$, for which no spectroscopic information has previously been reported.

EXPERIMENTAL

Xenon difluoride was prepared by u.v. irradiation of xenon-fluorine mixtures (mole ratio $Xe:F_2 > 1:1$)[6]. Xenon tetrafluoride was prepared by heating a mixture of xenon and fluorine (mole ratio 1:5) at 400°C and 6 atm, and purified using RuF_5 by the method of Bartlett and Sladky[7]. The adduct $XeF_2 \cdot XeF_4$ was prepared by fusing in a Kel-F trap an intimate mixture of equimolar amounts of the difluoride and tetrafluoride. The purity of the three compounds was checked by X-ray powder photography.

Raman spectra were obtained from finely powdered samples packed in thin-walled quartz capillaries of internal diameter ca. 1 mm. The capillaries were filled in the dry-nitrogen atmosphere of a VAC Dri-Lab, temperarily stoppered with Halocarbon grease, removed from the Dri-Lab, and permanently sealed by drawing down in a small flame. Raman spectra were excited at 4880 Å with a CRL argon-ion laser (power at sample 300 mW); using 180° backscattering light collection, spectra were recorded with a Spex 1401 monochromator and a photon-counting detection system.

RESULTS AND DISCUSSION

Our Raman spectra of solid XeF_4 are shown in the Figure and enumerated in Table 1. Use of laser excitation exposed the region of low Raman shift to examination, so that our spectra are more complete than in the earlier account. The most striking feature is the observation of *four* relatively strong features between 500 and 560 cm^{-1}, in the region primarily associated with fundamentals in Xe-F stretching modes, rather than the two expected for the XeF_4 molecule of D_{4h} symmetry. Since there exist no suitable overtone or combination levels to account, either directly or

via Fermi resonance, for this multiplicity of lines, we believe it to be due to vibrational coupling between different XeF_4 molecules in the lattice, and have interpreted the rest of the spectrum from this premise.

Figure 1 table [illegible]

Xenon tetrafluoride crystallizes in the monoclinic space group $P2_1/n$ (isomorphous with point group C_{2h}), with two XeF_4 molecules per unit cell[8]. The xenon atom sites are centres of symmetry, and there are two non-equivalent pairs of fluorine atoms in each molecule. While the Xe-F bond lengths are equal within the stated experimental uncertainty, the space group demands that the molecular symmetry be C_{2h}. A factor group analysis of the unit cell is presented in Table 2. Since the XeF_4 molecules retain their centres of symmetry in the lattice, the $3A_g + 3B_g$ internal modes of the crystal derive from the *gerade* modes of the free molecule; likewise the $6A_u + 6B_u$ internal crystal modes derive from the *ungerade* molecular modes. Only *gerade* modes give Raman-active fundamentals.

Table 2 near here

Table 1 shows the assignment of the observed Raman spectrum, and the correlation of the *gerade* vibrations of the discrete D_{4h} XeF_4 molecule with the vibrations of the bimolecular C_{2h} unit cell. The lines at 551 and 543 cm^{-1} are the crystal B_g and A_g relatives of the molecular A_{1g} fundamental (554.3 cm^{-1}), corresponding respectively to the out-of-phase and in-phase motions of the two molecules in the unit cell; the pairs of lines at 506 and 503 cm^{-1} and 238 and 216 cm^{-1} likewise correspond to the ν_4 (B_{2g}) and ν_2 (B_{1g}) fundamentals of the free molecule. Other features are assigned as lattice modes, overtones, and combinations. As in the vapour-phase Raman spectrum, first overtones of modes with *ungerade* fundamentals are observed: the effects of intermolecular coupling are again apparent in the observation of two lines (at 599 and 588 cm^{-1}) deriving

from the overtones of the A_u and B_u crystal components of the A_{2u} fundamental (ν_2) which is found at 291 cm^{-1} in the gaseous infrared spectrum[2].

Changes in the relative intensities of the Raman lines between vapour and solid support this model. In the spectrum of the vapour ν_4 (B_{2g}) has about one-tenth the intensity of ν_1 (A_{1g});[7] that the 543 cm^{-1} and 503 cm^{-1} lines of the solid have nearly equal intensities is consistent with both being fundamentals in totally symmetric A_g modes.

The 1:1 adduct $XeF_2 \cdot XeF_4$ crystallizes in the space group $P2_1/c$, which is closely related to that of XeF_4. The unit cell contains two molecules each of XeF_2 and XeF_4, and each molecule (XeF_2 or XeF_4) is surrounded by four neighbours of its own kind and eight of the opposite kind. However, a layer structure can be recognised with alternate planes of XeF_2 and XeF_4 molecules.

The essentially molecular nature of the adduct is clearly supported by the Raman spectrum shown in the Figure and assigned in Table 1; details of the spectrum, however, are very different from those of pure XeF_4. The lines at 548 cm^{-1} and 219 cm^{-1}, clearly identified with the XeF_4 component, show no splitting or asymmetry even using slit widths 0.25 cm^{-1}; in XeF_4, these lines show splittings of 8 cm^{-1} and 22 cm^{-1}, respectively. It is, therefore, assumed that only one of the three lines at 503, 509 and 511 cm^{-1} is due to XeF_4, the other two arising from ν_1 of XeF_2 via intermolecular coupling. In assigning the frequencies the A_g and B_g components of the XeF_4 vibrations are adjudged coincident. The pattern of overtones and combinations closely resembles that of XeF_4.

It is at first sight surprising that intermolecular vibrational coupling between the XeF_4 molecules in $XeF_2 \cdot XeF_4$ is so small that it

escapes detection in the Raman active fundamentals, since the adduct is closely related in structure to the pure phase; it may be due solely to the greater separation between the XeF_4 molecules in the adduct. In $XeF_2 \cdot IF_5$ no coupling of XeF_2 or IF_5 vibrations is seen in the Raman spectrum[10].

ACKNOWLEDGMENTS

The author is indebted to Professor Neil Bartlett for providing experimental facilities for fluorine chemistry, and for helpful discussions, and to Dr. J. Sherer, United States Department of Agriculture, Western Regional Laboratory, for access to Raman spectroscopy facilities. The award of a Harkness Fellowship from the Commonwealth Fund is gratefully acknowledged. The work was otherwise supported by the United States Atomic Energy Commission.

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TABLE I: Raman Spectra of Solid XeF_4 and $XeF_2 \cdot XeF_4$

$XeF_4(s)$ $P2_1/n \equiv C_{2h}$			$XeF_4(g)$ [a,c] D_{4h}			$XeF_2 \cdot XeF_4(s)$ $P2_1/c \equiv C_{2h}$			$XeF_2(g)$ [a] $D_{\infty h}$	
cm^{-1}	Rel. Int.	Assignment [b]	cm^{-1}	Rel. Int.	Assignment	cm^{-1}	Rel. Int.	Assignment [b]	cm^{-1}	Assignment
1093,b	0.03	$\nu_1/\nu_4 + \nu_2/\nu_5$				~1095,b	<0.01	$\nu_1/\nu_5 + \nu_1/\nu_5$		
1050,b	0.08	$\nu_1/\nu_4 + \nu_2/\nu_5$				1049,b	<0.01	$\nu_1/\nu_5 + \nu_2/\nu_6/\nu_3/\nu_7$		
1011,b	<0.01	$\nu_2/\nu_5 + \nu_2/\nu_5$				1008,b	<0.01	$\nu_3/\nu_7 + \nu_3/\nu_7$		
730,b	<0.01	$\nu_2/\nu_5 + \nu_3/\nu_6$								
682	0.07	$\nu_1/\nu_4 + 132$								
599	0.27	[2 × 299]				598	0.04	[2 × 299]		
588	0.18	[2 × 294]				586	0.03	[2 × 293]		
551	26	$\nu_4(B_g)$	554.3	vs	$\nu_1(A_{1g})$	548	100	$\nu_1(A_g)$, $\nu_5(B_g)$		
543	100	$\nu_1(A_g)$								
506,sh	~35	$\nu_5(B_g)$	524	m	$\nu_2(B_{2g})$	511	91	$\nu_2(A_g)$, $\nu_6(B_g)$		
503	85	$\nu_1(A_g)$								
						508	79	$\nu_7(B_g)$	514.5	$\nu_1(\Sigma_g^+)$
						503	88	$\nu_3(A_g)$		
448	0.23	[2 × 224]	433	vw	$[2\nu_4]$	438	0.3	[2 × 219]		
						430	0.2	[2 × 215]		
365,b	0.02	$\nu_3/\nu_6 + 132$								
325,b	0.0.04	[2 × 162]	322	vw	$[2\nu_7]$	~325,b	0.06	[2 × 163]		
283,b	0.09	$\nu_3 + 60/74$								
238	2.9	$\nu_6(B_g)$	218	m	$\nu_3(B_{1g})$	219	5	$\nu_4(A_g)$, $\nu_8(B_g)$		
216	3.1	$\nu_3(A_g)$								
132	4.1	Lattice Vibrations				106	23	Lattice Vibrations		
101	6.0					92,sh	2			
80,sh	3					78	20			
74	14					62	33			
60	10									

(a) Ref. 1

(b) Bracketed assignments are overtones of ungerade fundamentals.

(c) Ungerade fundamentals of $XeF_4(g)$: 586, $\nu_6(e_u)$; 291, $\nu_2(a_{2u})$; 216, $\nu_4(b_{1u})$; 161, $\nu_{7(eu)}$: Ref. 1

TABLE II: Factor Group Analysis for XeF_4 and $XeF_2 \cdot XeF_4$

Compound	XeF_4	$XeF_2 \cdot XeF_4$
Lattice type	Monoclinic	Monoclinic
Space Group	$P2_1/n \equiv C_{2h}$	$P2_1/c \equiv C_{2h}$
Internal vibrations		
Stretches	$2A_g + 2B_g + 2A_u + 2B_u$	$3A_g + 3B_g + 3A_u + 3B_u$
Deformations	$A_g + B_g + 4A_u + 4B_u$	$A_g + B_g + 6A_u + 6B_u$
Lattice modes		
Translational	$3A_u + 3B_u$	$6A_u + 6B_u$
Rotational	$3A_g + 3B_g$	$5A_g + 5B_g$
Raman-active classes	A_g, B_g	A_g, B_g
Infrared-active classes	A_u, B_u	A_u, B_u

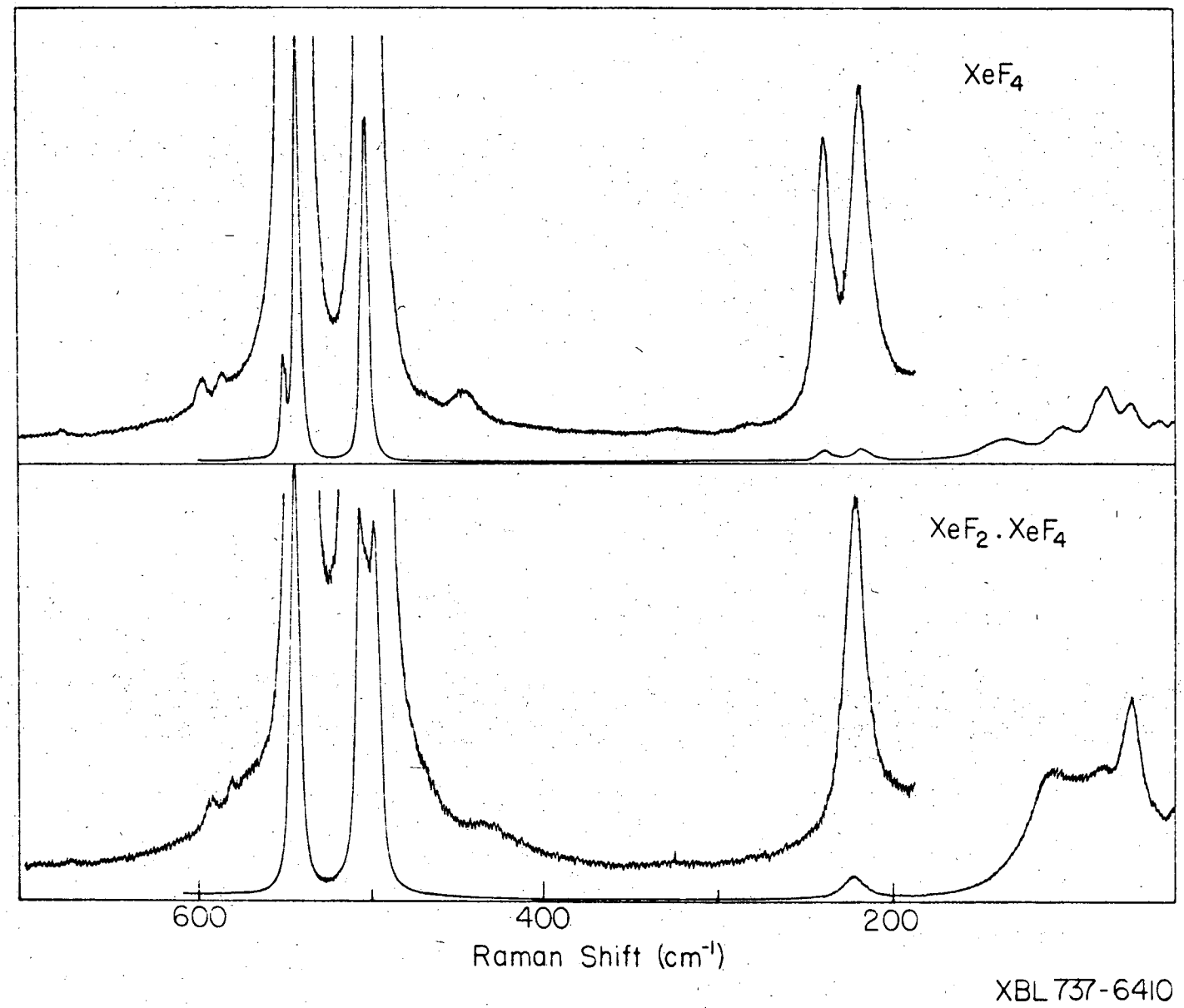

Fig. 1

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