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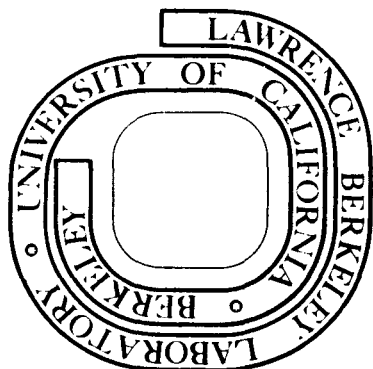
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THE RAMAN SPECTRA OF SOLID XENON TETRAFLUORIDE  
AND ITS ADDUCT WITH XENON DIFLUORIDE

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ABSTRACT

The Raman spectra of the solids  $\text{XeF}_4$  and  $\text{XeF}_2 \cdot \text{XeF}_4$  show effects arising in intermolecular vibrational coupling. Assignments based on factor group analysis are proposed.

INTRODUCTION

The Raman<sup>1</sup> and infrared<sup>2</sup> spectra of gaseous xenon tetrafluoride have previously and properly been interpreted in terms of a  $\text{XeF}_4$  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.*<sup>2</sup> observed only three Raman lines, which they assigned to fundamentals in the three Raman-active, *gerade* modes of a  $D_{4h}$   $\text{XeF}_4$  species:  $543 \text{ cm}^{-1}$ ,  $\nu_1$  ( $A_{1g}$ );  $502 \text{ cm}^{-1}$ ,  $\nu_4$  ( $B_{2g}$ );  $235 \text{ cm}^{-1}$ ,  $\nu_3$  ( $B_{1g}$ ).

During recent investigations made in this laboratory of complex formation between xenon tetrafluoride and antimony pentafluoride<sup>3-5</sup>, 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  $\text{XeF}_2 \cdot \text{XeF}_4$ , 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<sub>2</sub> > 1:1)<sup>6</sup>. 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<sub>5</sub> by the method of Bartlett and Sladky<sup>7</sup>. The adduct XeF<sub>2</sub>·XeF<sub>4</sub> 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, temporarily 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<sub>4</sub> 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<sup>-1</sup>, in the region primarily associated with fundamentals in Xe-F stretching modes, rather than the two expected for the XeF<sub>4</sub> molecule of D<sub>4h</sub> 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<sub>4</sub> molecules in the lattice, and have interpreted the rest of the spectrum from this premise.

Figure  
Table  
near here

Xenon tetrafluoride crystallizes in the monoclinic space group  $P2_1/n$  (isomorphous with point group  $C_{2h}$ ), with two XeF<sub>4</sub> molecules per unit cell<sup>8</sup>. 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<sub>4</sub> 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<sub>4</sub> molecule with the vibrations of the bimolecular  $C_{2h}$  unit cell. The lines at 551 and 543 cm<sup>-1</sup> are the crystal  $B_g$  and  $A_g$  relatives of the molecular  $A_{1g}$  fundamental (554.3 cm<sup>-1</sup>), 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<sup>-1</sup> and 238 and 216 cm<sup>-1</sup> likewise correspond to the  $\nu_4$  ( $B_{2g}$ ) and  $\nu_2$  ( $B_{1g}$ ) 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<sup>-1</sup>) deriving

from the overtones of the  $A_u$  and  $B_u$  crystal components of the  $A_{2u}$  fundamental ( $\nu_2$ ) which is found at  $291 \text{ cm}^{-1}$  in the gaseous infrared spectrum<sup>2</sup>.

Changes in the relative intensities of the Raman lines between vapour and solid support this model. In the spectrum of the vapour  $\nu_4$  ( $B_{2g}$ ) has about one-tenth the intensity of  $\nu_1$  ( $A_{1g}$ );<sup>7</sup> that the  $543 \text{ cm}^{-1}$  and  $503 \text{ cm}^{-1}$  lines of the solid have nearly equal intensities is consistent with both being fundamentals in totally symmetric  $A_g$  modes.

The 1:1 adduct  $\text{XeF}_2 \cdot \text{XeF}_4$  crystallizes in the space group  $P2_1/c$ , which is closely related to that of  $\text{XeF}_4$ . The unit cell contains two molecules each of  $\text{XeF}_2$  and  $\text{XeF}_4$ , and each molecule ( $\text{XeF}_2$  or  $\text{XeF}_4$ ) 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  $\text{XeF}_2$  and  $\text{XeF}_4$  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  $\text{XeF}_4$ . The lines at  $548 \text{ cm}^{-1}$  and  $219 \text{ cm}^{-1}$ , clearly identified with the  $\text{XeF}_4$  component, show no splitting or asymmetry even using slit widths  $0.25 \text{ cm}^{-1}$ ; in  $\text{XeF}_4$ , these lines show splittings of  $8 \text{ cm}^{-1}$  and  $22 \text{ cm}^{-1}$ , respectively. It is, therefore, assumed that only one of the three lines at  $503$ ,  $509$  and  $511 \text{ cm}^{-1}$  is due to  $\text{XeF}_4$ , the other two arising from  $\nu_1$  of  $\text{XeF}_2$  via intermolecular coupling. In assigning the frequencies the  $A_g$  and  $B_g$  components of the  $\text{XeF}_4$  vibrations are adjudged coincident. The pattern of overtones and combinations closely resembles that of  $\text{XeF}_4$ .

It is at first sight surprising that intermolecular vibrational coupling between the  $\text{XeF}_4$  molecules in  $\text{XeF}_2 \cdot \text{XeF}_4$  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  $\text{XeF}_4$  molecules in the adduct. In  $\text{XeF}_2 \cdot \text{IF}_5$  no coupling of  $\text{XeF}_2$  or  $\text{IF}_5$  vibrations is seen in the Raman spectrum<sup>10</sup>.

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TABLE I: Raman Spectra of Solid XeF<sub>4</sub> and XeF<sub>2</sub>·XeF<sub>4</sub>

XeF <sub>4</sub> (s)			XeF <sub>4</sub> (g) (a),(c)			XeF <sub>2</sub> ·XeF <sub>4</sub> (s)			XeF <sub>2</sub> (g) (a)	
cm <sup>-1</sup>	Rel. Int.	P2 <sub>1</sub> /n ≡ C <sub>2h</sub> Assignment (b)	cm <sup>-1</sup>	Rel. Int.	D <sub>4h</sub> Assignment	cm <sup>-1</sup>	Rel. Int.	P2 <sub>1</sub> /c ≡ C <sub>2h</sub> Assignment (b)	cm <sup>-1</sup>	D <sub>∞h</sub> Assignment
1095,b	0.03	v <sub>1</sub> /v <sub>4</sub> + v <sub>2</sub> /v <sub>5</sub>				~1095,b	<0.01	v <sub>1</sub> /v <sub>5</sub> + v <sub>1</sub> /v <sub>5</sub>		
1050,b	0.08	v <sub>1</sub> /v <sub>4</sub> + v <sub>2</sub> /v <sub>5</sub>				1049,b	<0.01	v <sub>1</sub> /v <sub>5</sub> + v <sub>2</sub> /v <sub>6</sub> /v <sub>3</sub> /v <sub>7</sub>		
1011,b	<0.01	v <sub>2</sub> /v <sub>5</sub> + v <sub>2</sub> /v <sub>5</sub>				1008,b	<0.01	v <sub>3</sub> /v <sub>7</sub> + v <sub>3</sub> /v <sub>7</sub>		
730,b	<0.01	v <sub>2</sub> /v <sub>5</sub> + v <sub>3</sub> /v <sub>6</sub>								
682	0.07	v <sub>1</sub> /v <sub>4</sub> + 132								
599	0.27	[2 × 299]				598	0.04	[2 × 299]		
588	0.18	[2 × 294]				586	0.03	[2 × 293]		
551	26	v <sub>4</sub> (B <sub>g</sub> )	554.3	vs	v <sub>1</sub> (A <sub>1g</sub> )	548	100	v <sub>1</sub> (A <sub>g</sub> ), v <sub>5</sub> (B <sub>g</sub> )		
543	100	v <sub>1</sub> (A <sub>g</sub> )								
506,sh	~35	v <sub>5</sub> (B <sub>g</sub> )	524	m	v <sub>2</sub> (B <sub>2g</sub> )	511	91	v <sub>2</sub> (A <sub>g</sub> ), v <sub>6</sub> (B <sub>g</sub> )		
503	85	v <sub>1</sub> (A <sub>g</sub> )				508	79	v <sub>7</sub> (B <sub>g</sub> )	514.5	v <sub>1</sub> (Σ <sub>g</sub> <sup>+</sup> )
						503	88	v <sub>3</sub> (A <sub>g</sub> )		
448	0.23	[2 × 224]	433	vw	[2v <sub>4</sub> ]	438	0.3	[2 × 219]		
						430	0.2	[2 × 215]		
365,b	0.02	v <sub>3</sub> /v <sub>6</sub> + 132								
325,b	0.004	[2 × 162]	322	vw	[2v <sub>7</sub> ]	~325,b	0.06	[2 × 163]		
283,b	0.09	v <sub>3</sub> + 60/74								
258	2.9	v <sub>6</sub> (B <sub>g</sub> )	218	m	v <sub>3</sub> (B <sub>1g</sub> )	219	5	v <sub>4</sub> (A <sub>g</sub> ), v <sub>8</sub> (B <sub>g</sub> )		
216	3.1	v <sub>3</sub> (A <sub>g</sub> )								
132	4.1					106	23			
101	6.0					92,sh	2	Lattice		
80,sh	3	Lattice				78	20	Vibrations		
74	14	Vibrations				62	33			
60	10									

(a) Ref. 1

(b) Bracketed assignments are overtones of ungerade fundamentals.

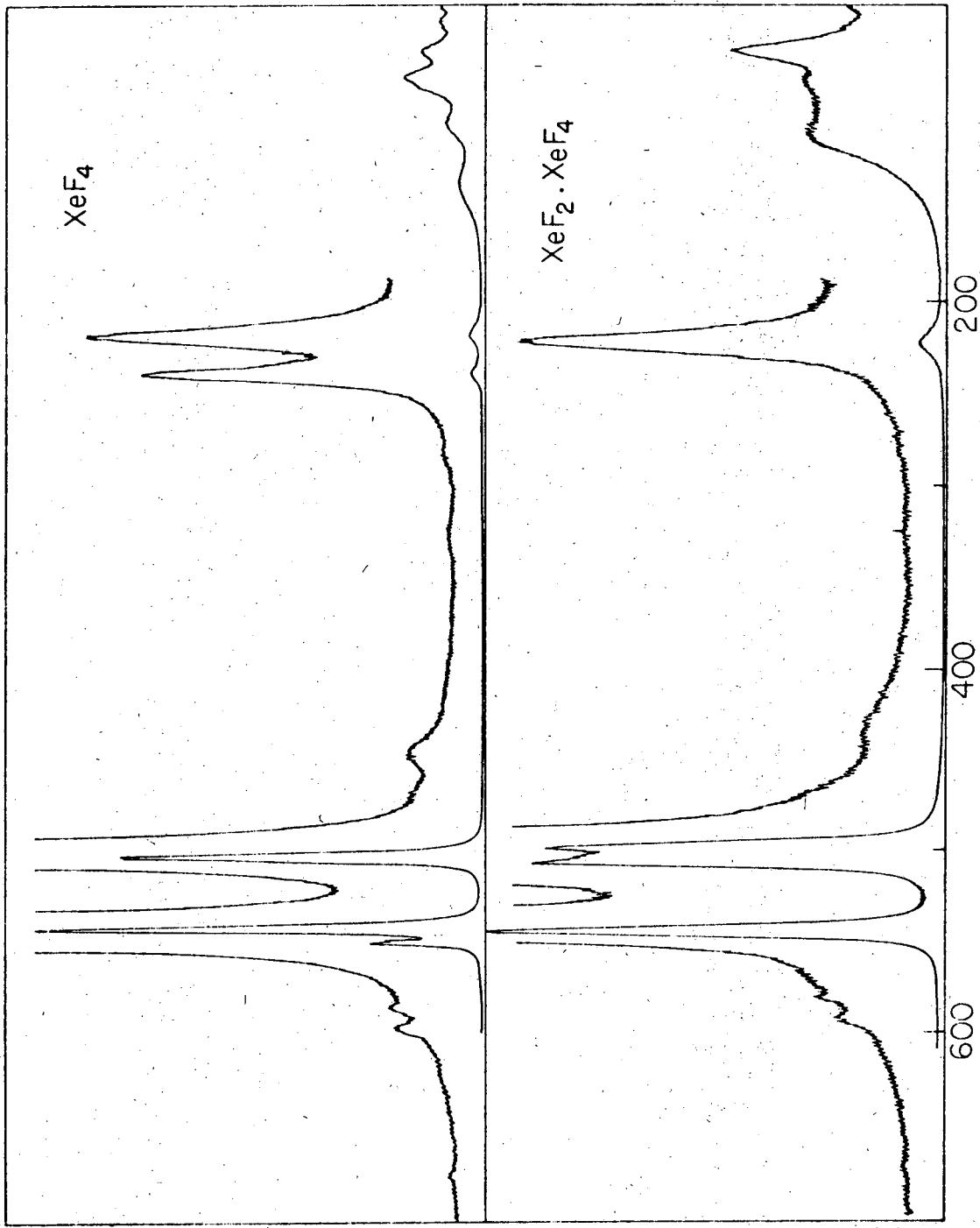
 (c) Ungerade fundamentals of XeF<sub>4</sub>(g): 586, v<sub>6</sub>(e<sub>u</sub>); 291, v<sub>2</sub>(a<sub>2u</sub>); 216, v<sub>4</sub>(b<sub>1u</sub>); 161, v<sub>7</sub>(e<sub>u</sub>): Ref. 1

4 1 1 0 6 9 0 0 0

TABLE II: Factor Group Analysis for  $\text{XeF}_4$  and  $\text{XeF}_2 \cdot \text{XeF}_4$

Compound	$\text{XeF}_4$	$\text{XeF}_2 \cdot \text{XeF}_4$
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	$A_u, B_u$	$A_u, B_u$

†



Raman Shift ( $\text{cm}^{-1}$ )

XBL 737-6410

Fig. 1

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