Vibrational Spectra and Structures of XeF_4 and $XeOF_4$.*

By Howard H. Claassen,** Cedric L. Chernick and John G. Malm

Argonne National Laboratory, Argonne, Illinois

CONF-126-9

Abstract

The infrared spectrum of XeF_4 vapor has strong bands at 123, 291, and 586 cm.$^{-1}$. The Raman spectrum of the solid has very intense peaks at 502 and 543 cm.$^{-1}$ and a weaker one at 235 cm.$^{-1}$. These data show that the molecule is planar and of symmetry D_{4h}. The seven fundamental frequencies have been assigned as 543 (a_{1g}), 291 (a_{2u}), 235 (b_{1g}), 221 (b_{1u}), 502 (b_{2g}), 586 (e_u), and 123 (e_u), the assignment of 221 cm.$^{-1}$ to b_{1u} being uncertain.

The infrared spectrum of $XeOF_4$ vapor has intense peaks at 288, 362, 578, 609, and 928.2 cm.$^{-1}$ and the Raman spectrum of the liquid has bands at 231, 286, 364, 530, 566, and 918 cm.$^{-1}$. The spectra fit a C_{4v} model very well. The fundamentals determined are: 928.2 (a_1), 578 (a_1), 288 (a_1), 231 (b_1), 530 (b_2), 609 (e), and 362 (e). This leaves

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

**Permanent address: Wheaton College, Wheaton, Illinois

Conference on Noble Gas Compounds
Argonne, Illinois
April 22-23, 1963

DISCLAIMER

one (b_2) and one (e) fundamental undetermined. Very close correspondence between vibrations in the two molecules indicates that the O-Xe-F angle in $XeOF_4$ must be rather close to 90°.

Introduction

The preparation of XeF_4 has been described previously (1) and the results of a preliminary study of its vibrational spectra reported briefly. (2) The preparation of $XeOF_4$ is described in the present volume. (3) We report here the results of a more complete study of the Raman spectrum of solid XeF_4 and of the infrared spectrum of the vapor. For $XeOF_4$ we have studied the Raman spectrum of the liquid and the infrared spectrum of the vapor.

Purity of Compounds

The purity of the XeF_4 was checked by infrared analysis. The probable impurities are XeF_6 and XeF_2 which have absorption peaks at 610 $cm.^{-1}$ and 566 $cm.^{-1}$ respectively. The sample was found to contain small amounts of the more volatile XeF_6 but this was easily removed since its vapor pressure is higher by a factor of 10. Pumping the equilibrium vapor rapidly out of the storage can several times removed the XeF_6 so that none of the 610 $cm.^{-1}$ absorption could be detected in the bulk of sample remaining. The $XeOF_4$ was prepared by reacting XeF_6 with SiO_2 as described in this volume. The completion of the reaction

was indicated by the disappearance of the yellow color. It was purified from materials of lower volatility, such as XeF_4, by keeping the quartz bulb in which it had been prepared at -25°C. while pumping out the $XeOF_4$.

Techniques of Spectroscopy

The infrared spectra were obtained with a Beckman IR-7 with CsI and NaCl prisms and Perkin-Elmer 421 and 301 spectrophotometers.* The cells were made of nickel and were used with either AgCl or polyethylene windows. For $XeOF_4$, with a 30 mm. vapor pressure at room temperature, the usual 10 cm. path length was enough but for XeF_4 a 60 cm. absorbing path was also used.

The Raman spectrum of XeF_4 was obtained for the solid using the Cary 81 photoelectric instrument with the lens system designed for solids. The sample used was approximately one gram that had grown to a single crystal in a sealed quartz tube. The $XeOF_4$ was studied as the liquid at room temperature using a Pyrex Raman tube with seven mm. O.D. and filled to a length of three cm. Qualitative indications of polarization were obtained for the stronger bands of $XeOF_4$ by using Polaroid cylinders around the Raman tube.

---

*We are indebted to the Perkin-Elmer Corporation for the opportunity to use the 301 instrument at Norwalk, Connecticut, and to Charles Helms and Robert Anacreon for their help with the operation of that spectrophotometer.

Results and Interpretation

XeF_4.--Figure 1 shows tracings of the regions of the infrared spectrum where bands were observed, and Fig. 2 is a tracing of the Raman spectrum. Judging from their positions and intensities the three infrared bands at 123, 291 and 586 $cm.^{-1}$ are probably fundamentals. Of the four bands observed in the Raman spectrum the one at 442 $cm.^{-1}$ is the least intense and probably does not represent a fundamental. It may, in fact, represent a combination of 543 $cm.^{-1}$ excited by 4339 Å. and 502 $cm.^{-1}$ excited by 4347 Å. which would occur at apparent shifts of 442 and 445 $cm.^{-1}$ from 4358 Å.

In considering the information the spectral data furnish on the molecular symmetry, it must be noted that the Raman measurements are for the solid compound and the infrared ones are for the vapor. Some solid-vapor shifts in frequencies are to be expected and the Raman spectrum might contain frequencies due to lattice modes.

From the infrared spectrum alone one can conclude that there is high symmetry in the XeF_4 molecule. Only one band is observed in the region where bond stretching motions (500 - 700 $cm.^{-1}$) are expected. Of all the symmetries possible for the YZ_4-molecule, only for T_d(tetrahedral) and D_{4h}(square-planar) would there be just one infrared-active bond stretching fundamental. The infrared spectrum also allows the distinction to be made between

these two symmetries since a T_d molecule would have one bending mode that would be infrared active while a D_{4h} molecule would have two. As two are observed for XeF_4, the D_{4h} model is the preferred one. Strong support for this is provided in the Raman spectrum also.

The fundamental vibrations of a D_{4h} YZ_4 molecule are described in the left half of Fig. 3 as to their modes of atomic motions, symmetries, numbering and spectral activity. The assignment of ν_2 is definite from the band contours predicted for planar molecules by Gerhard and Dennison. (4) Only for the out-of-plane motion, ν_2, should there be a very intense Q-branch and this is observed at 291 $cm.^{-1}$. The other two infrared fundamentals are then assigned without ambiguity.

The Raman spectrum of the solid also fits very well. The two very intense bands at 543 and 502 $cm.^{-1}$ must be due to the two stretching vibrations. Although polarization measurements could not be made it is quite certain that the symmetric vibration is the higher one because any significant repulsion between fluorines would almost require this. Further support for this interpretation of the Raman spectrum of the solid has recently been obtained in this laboratory.* The 235 $cm.^{-1}$ Raman band is assigned

*H. H. Hyman and L. A. Quarterman observed a Raman band at 553 $cm.^{-1}$ of XeF_4 in HF solution. This must correspond to the 543 $cm.^{-1}$ band for the solid. The ν_5 band was not observed in the very dilute solution. This indicates that the higher frequency is a sharper band in the solution and is therefore the totally symmetric one.

to ν_3 without question. The band at 442 cm.$^{-1}$, if an actual frequency, must be an overtone of the inactive ν_4. This gives the value of 221 for ν_4, but this must be considered as quite doubtful and is therefore listed in Fig. 3 with two question marks.

The infrared absorption peaks at 1105 and 1136 cm.$^{-1}$ may be assigned as $\nu_5 + \nu_6 = 1088$ cm.$^{-1}$ and $\nu_1 + \nu_6 = 1129$ cm.$^{-1}$ The fit is satisfactory when account is taken of corrections needed due to vapor to solid shift of frequencies.

There is one feature of the infrared spectrum that we do not understand and that is the doublet appearance of ν_6. This has been traced many times and the peaks reproducibly found at 581 and 591 cm.$^{-1}$. Expected is a triplet band with all three peaks of about equal intensity and with a P-R separation of approximately 14 cm.$^{-1}$. (4) The observed splitting is much too large to ascribe to isotopes of xenon and may be due to a Coriolis coupling between the doubly degenerate vibration and rotation.

The structure of XeF_4 solid has been obtained by X-ray diffraction (5,6,7) and by neutron diffraction.(8) It has been found that the molecule is square planar within experimental error. Confirmation of the square planar molecule in the vapor phase has been obtained by electron diffraction. (9)

Several theoretical discussions (10,11) have stated

that the square planar model best fits the theory and one of them (10) suggests that the molecule could possibly be distorted by coulomb repulsion. Therefore, it seems interesting to question whether the vibrational data require an exactly planar molecule or whether the "ring" of fluorines might be slightly puckered. If the latter were true the Raman-active ν_5 would be infrared-active, but a slight distortion would, of course, result in a very weak infrared band. One can set a rough upper limit to the amount of possible puckering if one looks at the infrared spectrum in the region of 502 cm.$^{-1}$ and makes the plausible assumption that the rate of change of bond moment with stretching is approximately the same for ν_5 and ν_6. The result is that an upper limit can be set for deviation of the Xe-F bond from the plane of about 0.5 degrees, or fluorine distances of 0.02 Å. from the plane.

The Q-R separation of 11 ± 1 cm.$^{-1}$ in the 291 cm.$^{-1}$ band can be used to calculate a bond length. This gives 1.85 ± 0.2 Å. for the Xe-F bond, in good agreement with the value of 1.94 Å. for the vapor obtained from electron diffraction. (9) Since the value of ν_4 is uncertain, we have not calculated thermodynamic functions.

$XeOF_4$.--Figure 4 is a tracing of the infrared spectrum of $XeOF_4$ vapor and Fig. 5 is a photograph of the Raman spectrum of the liquid. The intense absorption band at 928.2 cm.$^{-1}$ for the vapor and the peak at 919 cm.$^{-1}$ in the

Raman of the liquid must represent a Xe = O stretching motion. The high value of this frequency rules out the possibility that the O is bonded to both Xe and one of the fluorines. Rather, the valence of the Xe is six, and the most likely molecular symmetry then is C_{4v}, which is adequately verified by the spectra. The right half of Fig. 3 gives the spectral activity, our assignments, the species and schematic indications of vibrational motions of $XeOF_4$ assuming C_{4v} symmetry. The XeF_4 part of the molecule is drawn in the figures as plane although the symmetry does not require this. The two Raman bands with no counterparts in the infrared must be assigned to b species, and can be identified with ν_4 and ν_5 by comparison with corresponding motions in the XeF_4 molecule. The polarization scans indicated that both 919 $cm.^{-1}$ and 566 $cm.^{-1}$ are polarized and therefore must be assigned to a_1. The identical and distinctive shapes of the infrared bands at 928.2 and 288 $cm.^{-1}$ indicate that they belong to the same species, so the 288 $cm.^{-1}$ is assigned also to a_1. The 566 (a_1) is the most intense Raman band and probably has its infrared counterpart at 578 $cm.^{-1}$, where its sharp Q-branch is seen on the side of an intense band. It is the weakest of the infrared fundamentals.

The two other strong infrared bands then must be e fundamentals. They are assigned as ν_7 and ν_8 because ν_9 is expected to be lower in frequency. This leaves ν_6 and

ν_9 undetermined. The former may be described as an "F_4 ring puckering" motion that is probably very weak in the Raman effect; the corresponding motion in XeF_4, ν_4, is inactive. A search was made for ν_9 between 100 and 200 cm.$^{-1}$ in the Raman spectrum. The scans are not shown in Fig. 5 because no band was found. It may be expected to be very weak in the Raman because the corresponding vibration in XeF_4 is active only in the infrared. When ν_9 has been obtained by extending the infrared study to lower frequencies, and the heat capacity of $XeOF_4$ has been measured, it should be possible to calculate an approximate value for ν_6.

Three weak bands in the infrared and one in the Raman may be assigned as combinations. The infrared bands at 1186, 1156 and 735 cm.$^{-1}$ are assigned as $\nu_2 + \nu_7 = 1187$ (E), $2 \times \nu_2 = 1156(A_1)$ and $2 \times \nu_8 = 724(A_1+B_1+B_2)$. The last one is also close to expected values for $\nu_7 + \nu_9$ $(A_1+A_2+B_1+B_2)$ and $\nu_5 + \nu_6(A_1)$. The weak Raman band at 818 cm.$^{-1}$ is assigned as $\nu_3 + \nu_5 = 816(B_2)$.

Comparisons of the Two Molecules

As is indicated in Fig. 3, there is a close correspondence between the vibrations of XeF_4 and those of $XeOF_4$. Each vibration of XeF_4 has a corresponding one in $XeOF_4$ and the latter has two additional ones. There is only one pair, however, for which frequencies can be compared directly between the two molecules because only for

ν_3 in XeF_4 and ν_4 in $XeOF_4$ do we have comparable motions and each is the only vibration in the species so that there are no interactions with other vibrations. For this pair we have 235 $cm.^{-1}$ for solid XeF_4 and 231 for liquid $XeOF_4$, i.e. essentially the same frequency. Intensity comparisons provide further confirmation for the close correspondence. Thus ν_2 for $XeOF_4$ is very strong in the Raman and very weak in the infrared and the corresponding motion in XeF_4 is allowed only in the Raman spectrum. ν_6, ν_7 and ν_9 in $XeOF_4$ are all allowed in the Raman effect but not observed presumably because they are very weak. The three corresponding motions in XeF_4 are all forbidden in the Raman effect. These observations indicate that the XeF_4 part of the $XeOF_4$ has very nearly the same configuration as the XeF_4 molecule. Thus the O-Xe-F angle must be rather near 90° although the C_{4v} symmetry does not require 90° and repulsion between the oxygen and the fluorines could well cause a larger angle.

Force Constants

Preliminary force constant calculations using a valence plus interaction terms type of potential function similar to that used by Claassen for hexafluorides (12) gave a value of 3.00 md/Å. for the bond stretching constant and 0.12 for the interaction constant between bonds at

right angles. The interaction constant for opposite bonds cannot be determined accurately, but is approximately 0.06 md/Å. These may be compared with values given by Smith (13) for XeF_2 and with those for PuF_6, (12) a molecule that also has fluorine bonds at right angles and of comparable bond length.

Molecule	XeF_4	XeF_2	PuF_6
Bond length	1.94 Å.(8)	2.00 A.(14)	1.972 (12)
Stetching force constant	3.00 md/Å.	2.85 md/Å.	3.59 md/Å.
Interaction constant for perpendicular bonds	0.12	-	0.22
Interaction constant for opposite bonds	~0.06	0.11	-0.08

5-8-63/jcw

References

1. H. H. Claassen, H. Selig and J. G. Malm, J. Am. Chem. Soc. 84, 3593 (1962).
2. C. L. Chernick, et al., Science, 138, 136 (1962).
3. C. L. Chernick, H. H. Claassen, J. G. Malm and P. L. Plurien, page --- (on $XeOF_4$ prep.)
4. S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933).
5. J. A. Ibers and W. E. Hamilton, Science, 139, 106 (1963) (also page --- XRD on XeF_4).
6. D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, J. Am. Chem. Soc. 85, 242 (1962) (also page ---, XRD on XeF_4).
7. S. Siegel and E. Gebert, Ibid. 85, 240 (1963).
8. J. H. Burns, P. A. Agron and H. A. Levy, Science, 139, 1209 (1963) (also page --- N. Diff on XeF_4)
9. R. K. Bohn, K. Katada, J. V. Martinez and S. H. Bauer, (page ---).
10. R. E. Rundle, J. Am. Chem. Soc. 85, 112 (1963).
11. L. L. Lohr, Jr. and W. N. Lipscomb, Ibid., 85, 240 (1963).
12. H. H. Claassen, J. Chem. Phys. 30, 968 (1959).
13. D. F. Smith, Ibid., 38, 270 (1963).
14. H. A. Levy and P. A. Agron, J. Am. Chem. Soc. 85, 241 (1963).

Fig. 1. Infrared spectrum of XeF_4 vapor. Approximately 3 mm. pressure.

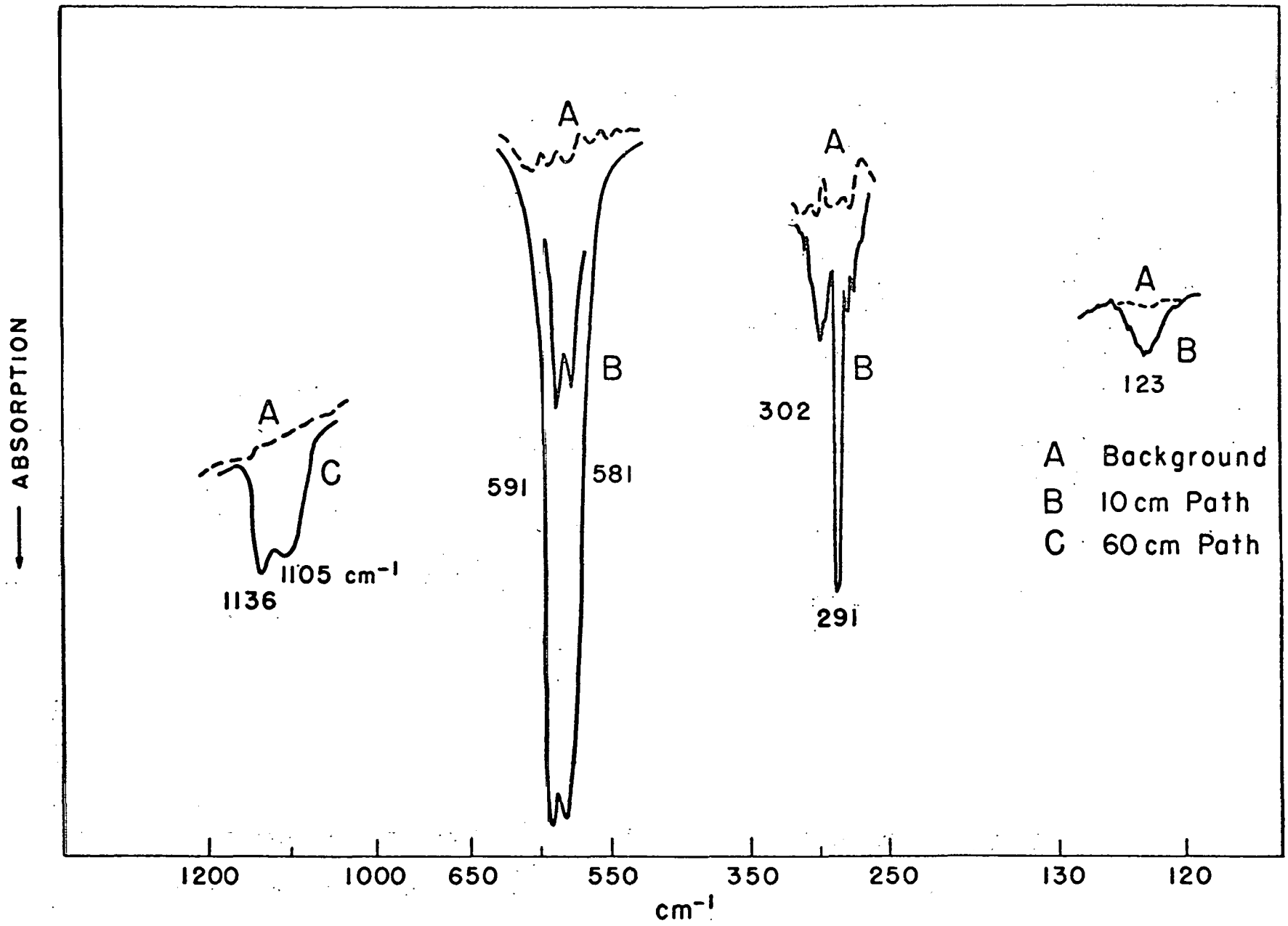

ABSORPTION
A
C
1105 cm⁻¹
1136
A
B
591
581
A
B
302
291
A
B
123
A Background
B 10 cm Path
C 60 cm Path
1200
1000
650
550
350
250
130
120
cm⁻¹

Fig. 2. Raman spectrum of solid XeF_4.

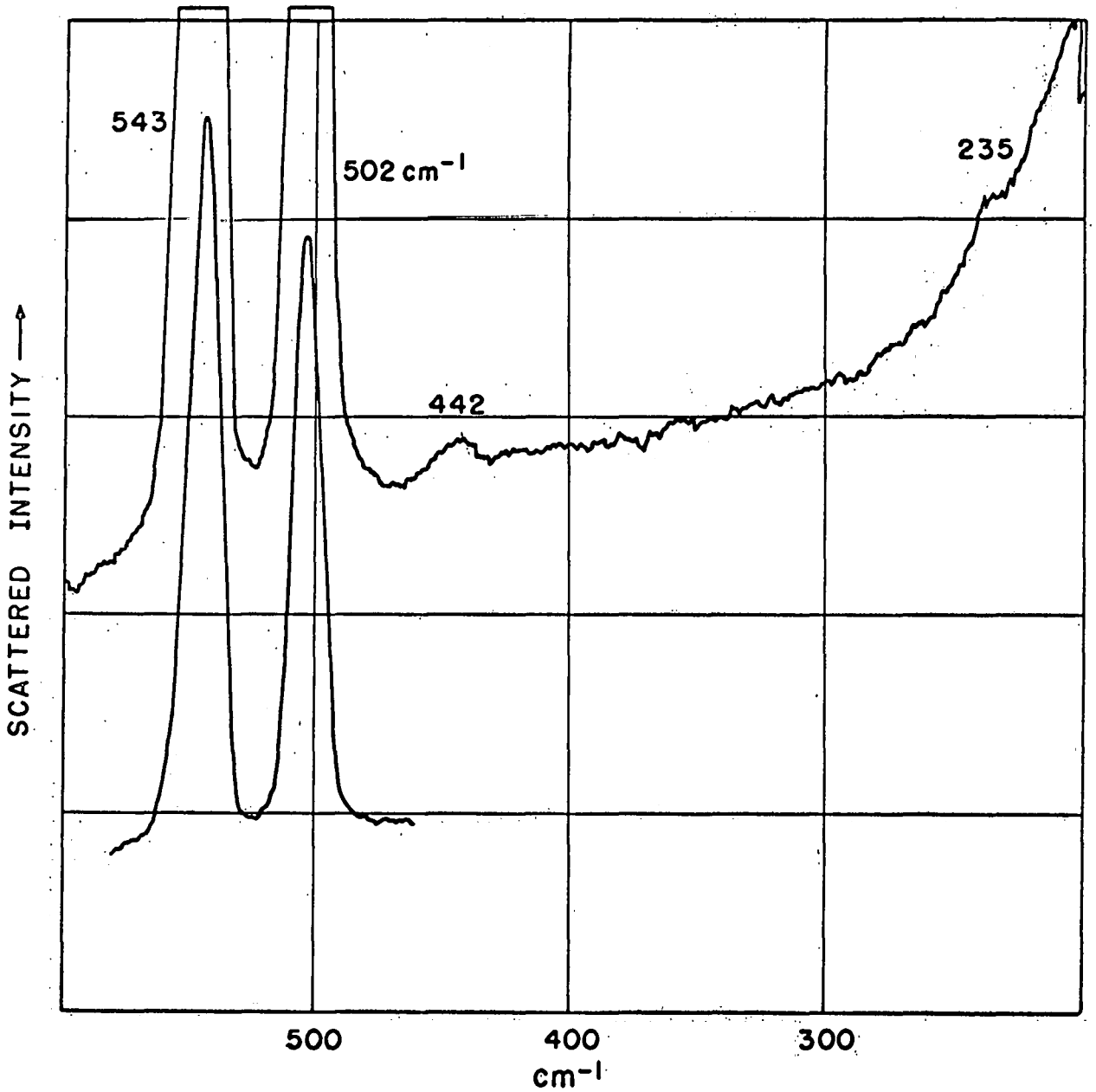
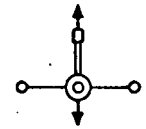
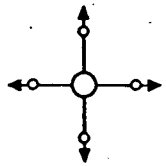
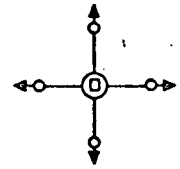
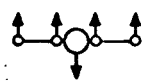
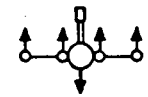
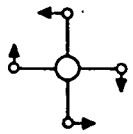
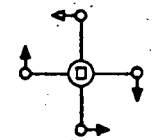
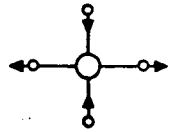
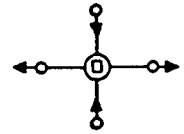
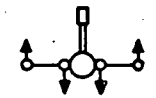
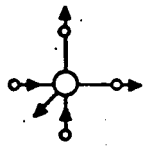
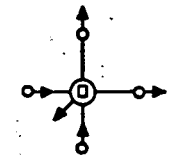
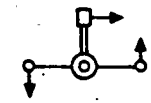
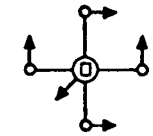

543
502 cm⁻¹
442
235
SCATTERED INTENSITY
500
400
300
cm⁻¹

Fig. 3. Vibrational modes and assignments for XeF_4 and $XeOF_4$.

XeF_4					$XeOF_4$			
					R,p 919 s IR 928.2 s	ν_1	a_1	
	a_{1g}	ν_1	R	543 vs	R,p 566 vs IR 578 ? vw	ν_2	a_1	
	a_{2u}	ν_2	IR	291 s	R 286 vw IR 288 s	ν_3	a_1	
	b_{1g}	ν_3	R	235 w	R 231 w	ν_4	b_1	
	b_{2g}	ν_5	R	502 vs	R 530 s	ν_5	b_2	
	b_{1u}	ν_4	Inactive 221 ??		R n.o. –	ν_6	b_2	
	e_u	ν_6	IR	586 vs	R n.o. – IR 609 vs	ν_7	e	
					R 364 mw IR 362 ms	ν_8	e	
	e_u	ν_7	IR	123 w	R n.o. – IR n.o. –	ν_9	e	

120 7266

Fig. 4. Infrared spectrum of $XeOF_4$ vapor.

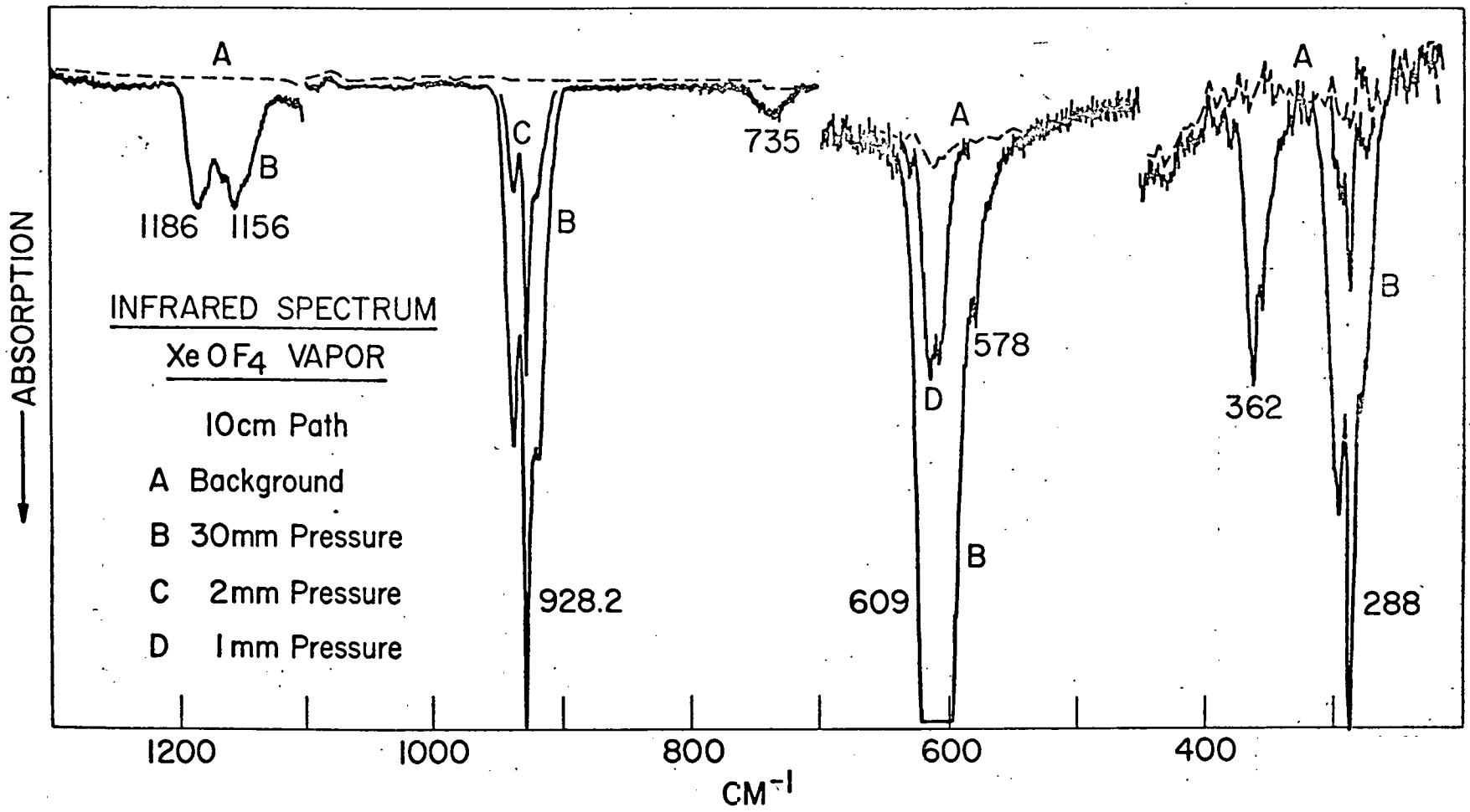
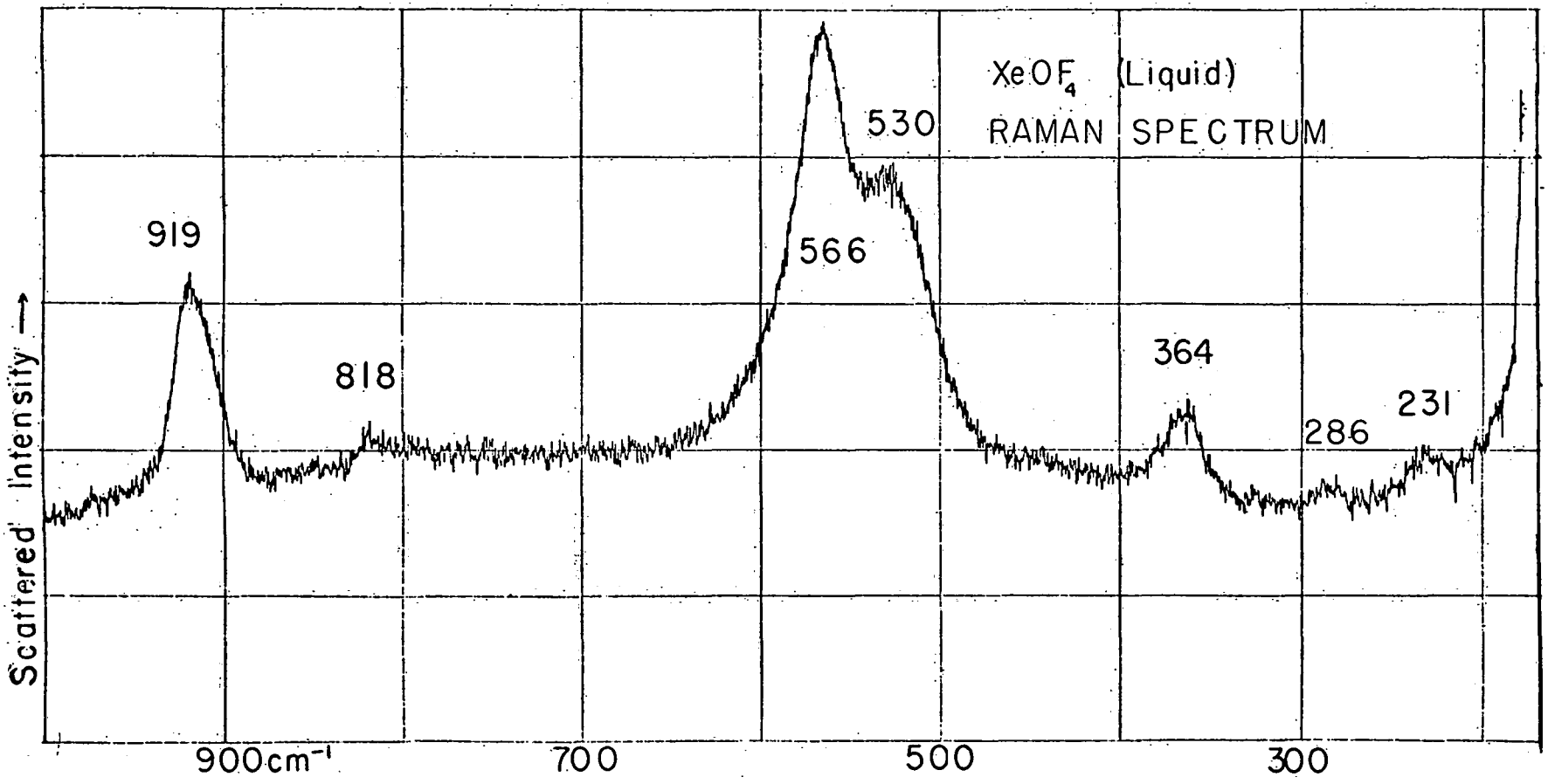

A
B
1186
1156
C
B
928.2
735
A
D
609
578
B
A
362
B
288
INFRARED SPECTRUM
Xe O F4 VAPOR
10cm Path
A Background
B 30mm Pressure
C 2mm Pressure
D 1mm Pressure
ABSORPTION
1200
1000
800
600
400
CM-1

Fig. 5. Raman spectrum of liquid $XeOF_4$.


XeOF4 (Liquid)
RAMAN SPECTRUM
919
818
566
530
364
286
231
Scattered Intensity →
900cm⁻¹
700
500
300