Vibrational Spectra and Structure of Xenon Tetrafluoride[1]

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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 weaker ones at 235 and 442 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 (b_{1u}) frequency value is quite uncertain.

Introduction

The preparation of XeF_4 has been described previously[3] and the results of a preliminary study of its vibrational spectra reported briefly.[4] We report here the results of a more complete study of the Raman spectrum of the solid phase and the infrared spectrum of the vapor.

Experimental Procedures

Preparation.—The purity of the XeF_4, prepared as described elsewhere,[3] was checked by infrared analysis. The probable impurities are XeF_6 and XeF_2 which have absorption peaks at 612 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 612 cm.$^{-1}$ absorption could be detected in the bulk of sample remaining.

Infrared Spectra.—The vapor pressure of XeF_4 (approximately 2 mm. at 20°) was sufficient to allow the observation of the fundamentals at or slightly above room temperature in a 10-cm. cell. For weaker bands a 60-cm. absorbing path was obtained by use of the mirror cell designed at this Laboratory and previously described.[5] The cells were made of nickel and were used with either AgCl or polyethylene windows. The spectra were obtained with a Beckman IR-7 with CsI prism and Perkin–Elmer 421 and 301 spectrophotometers. We are indebted to the Perkin–Elmer Corporation for the opportunity to use the 301 instrument at Norwalk, Conn., and to Charles Helms and Robert Anacreon for their help with the operation of that spectrophotometer.

The reproducibility of the spectrum and uniform composition of the sample were established by scanning several samples. A nickel can containing about 1 g. of XeF_4 was connected to the cell and to a similar can. The whole sample was transferred batchwise to the second can and vapor samples of each batch were taken into the cell. In most cases just the two most intense bands were examined to look for possible changes which would be indicative of impurities, but several complete spectra were also observed.

Raman Spectra.—The sample used was approximately 1 g. of XeF_4 that had grown to a single crystal in a sealed quartz tube. The spectrum was obtained using a Cary 81 photoelectric instrument with the lens system designed for solids.

Results and Interpretation

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 may not represent a fundamental. In fact, the reality of the 442 cm.$^{-1}$ frequency is doubtful since the 543 cm.$^{-1}$ vibration excited by 4339 Å. and the 502 cm.$^{-1}$ one excited by 4337 Å. would occur at apparent shifts of 442 and 445 cm.$^{-1}$, respectively, 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.

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 occur (500–700 cm.$^{-1}$). Of all the symmetries possible for a 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 Fig. 3 as to their symmetries, numbering, spectral activity and modes of atomic motions. The assignment of ν_2 is definite from the band contours expected according to Gerhard and Dennison.[6] 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 fits very well and lends strong support for the planar model. 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.[7] The 235 cm.$^{-1}$ Raman band is then assigned to ν_3 and this leaves 442 cm.$^{-1}$ to be assigned. If the band is real it cannot be a fundamental and it must be an overtone or combination band and the only plausible assignment is that it is $2\nu_4$. This gives the value of 221 cm.$^{-1}$ for ν_4 that is listed with a question mark since the assignment is not certain. 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.$^{-1}$.[6] The observed splitting is much too large to ascribe to isotopes of xenon, and may be due to a Corio-

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(3) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(4) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(5) B. Weinstock, H. H. Claassen and C. L. Chernick, *J. Chem. Phys.*, **38**, 1470 (1963).

(6) S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933).

(7) 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_1 band was so broadened, however, that it was not definitely observed in the very dilute solution. That the higher frequency band remained sharp is good indication that it represents the totally symmetric vibration.
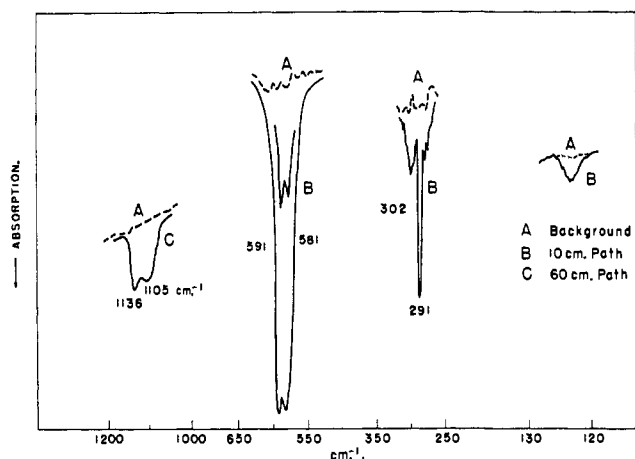
Fig. 1.—Infrared spectrum of XeF₄ vapor.
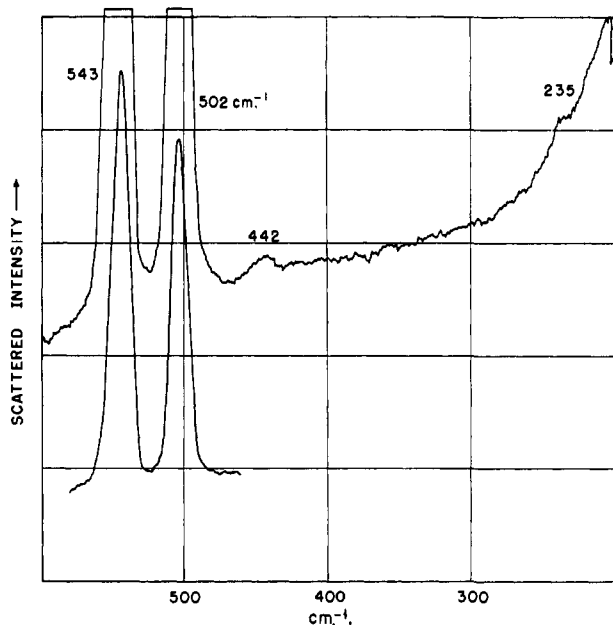
Fig. 2.—Raman spectrum of solid XeF₄.

lis coupling between the doubly degenerate vibration and rotation.

The structure of XeF₄ has been obtained by X-ray diffraction by Ibers and Hamilton.[8]   They find that for the solid, also, the molecule is square planar within experimental error.

Several theoretical discussions[9]−[11] have stated that the square planar model best fits the theory and one of them[9] 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

Xe F₄ Fundamentals

(D₄ₕ Symmetry)

Fig. 3.—Numbering, spectral activity, and assignment of fundamentals.

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 degree, 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 1.92 Å. for the solid obtained from X-ray diffraction.[8]   Since a more precise value of the bond length for the vapor molecule will probably be available soon from electron diffraction studies, we have not calculated thermodynamic functions.

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 mdynes/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 mdyne/Å.   These may be compared with values given by Smith[13] for XeF₂ and with those for PuF₆,[12] a molecule that also has fluorine bonds at right angles and a comparable bond length.

Molecule	XeF₄	XeF₂	PuF₆
Bond length, Å.	1.92[8]	2.00[14]	1.972
Stretching force constant, mdynes/Å.	3.00	2.85	3.59
Interaction constant for perpendicular bonds	0.12	..	0.22
Interaction constant for opposite bonds	~0.06	0.11	−0.08

(8) J. A. Ibers and W. C. Hamilton, Science, 139, 106 (1963).

(9) R. E. Rundle, J. Am. Chem. Soc., 85, 112 (1963).

(10) L. L. Lohr and W. N. Lipscomb, ibid., 85, 240 (1963).

(11) L. C. Allen, Science, 138, 892 (1962).

(12) H. H. Claassen, J. Chem. Phys., 30, 968 (1959).

(13) D. F. Smith, ibid., 38, 276 (1963).

(14) P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. F. Jones and D. F. Smith, Science, 139, 842 (1963).