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Far-Infrared and Millimeter Wave Studies of Xenon Hexafluoride[1a]

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Of the three binary fluorides, the oxytetrafluoride, and the tetroxide of xenon that have been studied in gas phase, only the XeF_6 structure has not yet been determined. Gas-phase electron diffraction,[2-4] Raman,[5] and infrared[6] studies have been made, but these have not led to a definite structure. The valence-shell electron-pair repulsion concept[7] predicts the XeF_6 structure to be considerably distorted from the O_h symmetry since the nonbonding electron pair occupies one of the seven coordination sites. On the other hand, the predictions of the semiempirical molecular orbital calculations[8,9] have not given an unequivocal prediction as to the equilibrium structure. A recent molecular beam study[10] set the upper limit of 0.03 D for the static dipole moment of XeF_6, thus eliminating the pair repulsion model. More recently Bartell[9] proposed a model in which the f_{1u} bending potential is a double minimum type, having a relatively high barrier, but owing to the triply degenerate character of the f_{1u} mode the inversion levels lie quite low. It was predicted that the first transition of the inversion levels would be about an energy of 6 cm^{-1}. We report here the far-infrared spectrum of XeF_6 and an attempt to observe the inversion lines in the millimeter wave region.

The infared spectrum of XeF_6 has previously been investigated in the region above 400 cm^{-1}.[6] In this region, only one fundamental, the f_{1u} stretching mode, is expected if the molecule XeF_6 has O_h symmetry. Instead two distinct absorption maxima at 613 and 520 cm^{-1} were reported. Also a considerable absorption was noted between the two peaks. We have recently reexamined this region carefully and found a definite third peak at 563 cm^{-1}. A broad absorption reported previously at 1100 cm^{-1} also shows structures at 1036, 1075, and 1118 cm^{-1}. The infrared spectrum of this region is shown in Figure 1.

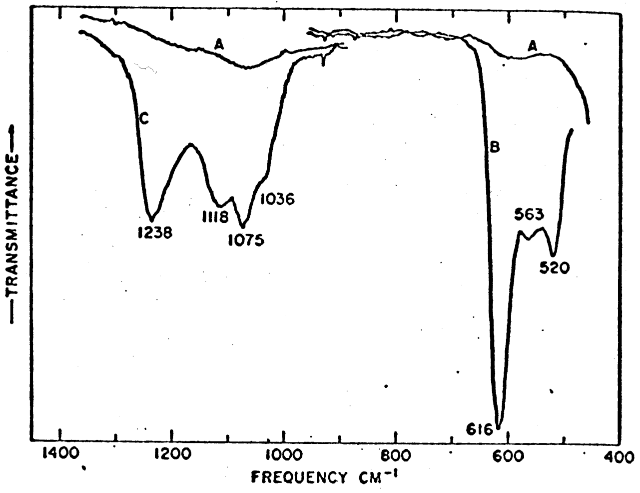

Figure 1.—Infrared spectrum of gaseous XeF_6 at room temperature: A, background; B, 10-cm cell, vapor pressure at −10°; C, 60-cm path cell, vapor pressure at 10°.

The bond-bending vibrational modes are expected to have frequencies below 300 cm^{-1}. Only one of these (f_{1u}) will be active in the infrared spectrum if the molecule has the high symmetry O_h. This region has not been studied previously owing to experimental difficulty. The commonly used far-infrared window materials (polyethylene, CsI, quartz, silicon, etc.) react readily with XeF_6. However, we used polyethylene windows coated with a thin film of Kel-F grease and found that it withstood attack of XeF_6 vapor at room temperature for several hours. The absorption cell was made of nickel and has a path length of 60 cm.[11] When the cell with the Kel-F grease coated polyethylene window was aligned to the Perkin-Elmer 301 spectrophotometer, 20% power transmission was obtained. The cell was filled with a room-temperature vapor pressure of pure XeF_6[12] and a search was made for absorption bands in the region of 40 to 400 cm^{-1}. No distinct absorption band was observed, except weak HF impurity lines. The amount of HF impurity in the XeF_6 sample was determined to be less than 0.05 mm (~0.2%). Instead of an absorption band as expected for a molecule having O_h symmetry, we observed a broad absorption starting at about 100 cm^{-1} and extending to the base of 520-cm^{-1} lines, without a distinguishable maximum.

Because no maxima were observed and because there was a slow drift in the base line of the spectrophotometer, we resorted to measuring the per cent power absorption at 25-cm^{-1} intervals. The XeF_6 gas was frozen into the side arm attached to the cell and the single-beam power was adjusted to 100% by opening

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(2) R. K. Bohn, K. Katada, J. V. Martinez, and S. H. Bauer, presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963.

(3) L. S. Bartell, R. M. Gavin, Jr., H. B. Thompson, and C. L. Chernick, *J. Chem. Phys.*, 43, 2517 (1965).

(4) K. Hedberg, S. H. Peterson, R. R. Ryan, and B. Weinstock, *ibid.*, 44, 1726 (1966).

(5) E. L. Gasner and H. H. Claasen, in press.

(6) D. F. Smith, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 300; H. H. Claassen, "The Noble Gases," D. C. Heath and Co., Boston, Mass., 1966, p 93.

(7) R. J. Gillespie, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 333.

(8) E. A. Boudreaux, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 351; L. L. Lohr, Jr., and W. N. Lipscomb, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 347.

(9) L. S. Bartell, *J. Chem. Phys.*, 46, 4530 (1967).

(10) W. E. Falconer, A. Büchler, J. L. Stauffer, and W. Klemperer, unpublished work.

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

(12) Calorimetric sample used in the work of J. G. Malm, F. Schreiner, and D. W. Osborne, *Inorg. Nucl. Chem. Letters*, 1, 97 (1965).

the slit, then the sample was introduced into the cell by warming the side arm. It took about 2–3 min for the beam power to reach a steady level. Then the side arm was again frozen to restore the power rapidly to the level of the empty cell. The results of the absorption measurements are given in Table I. Experimental uncertainties are ±1% unless otherwise stated. At 400 cm^{-1}, we are already observing the tail portion of the 520-cm^{-1} absorption. It is clear from Table I that the bending mode of XeF_6 must be quite different from those of other known hexafluorides, whose f_{1u} bending modes are sharp and absorption widths at the half-intensity height are normally less than 25 cm^{-1} at the pressure range of 20 mm. Furthermore, the P–Q–R branches are often well resolved at this pressure.

TABLE I

XeF_6 ABSORPTION IN FAR-INFRARED REGION

Freq, cm^{-1}	% power absorption	Freq, cm^{-1}	% power absorption
50	0 ± 3	175	11
75	1 ± 1	200	11
100	4	225	11
125	5	250	13
150	7	400	20

The millimeter wave spectrometer used for this study uses the principle of the free-space cell.[13] The cell is a nickel tube with a 2.5-in. inside diameter and a 5-ft length, with Teflon windows on the ends. The cell was seasoned with ClF_3 and then with XeF_6. The XeF_6 sample stored in the cell was transferred to an infrared cell several times during the investigation and spectra were taken to determine the purity of the sample. Only a small trace of $XeOF_4$ was observed as an impurity. We searched for millimeter wave absorption at room temperature with sample pressures ranging from 50 to 100 μ. The spectral region of 3.7–8.6 cm^{-1} was covered with the fourth, fifth, sixth, and seventh harmonics of the Oki klystrons, 35VII and 30VII. We have not observed any absorption line that can be attributed to the molecule XeF_6.

It is difficult to calculate or even predict the magnitude of the absorption coefficients of the inversion lines embodied in the Bartell model.[9] The sensitivity of the spectrometer is in the range of detecting a line with absorption coefficient greater than 10^{-5} cm^{-1}. The video detection method used sets an upper limit of 15 Mc for the width of absorption line to be detected. With this spectrometer we observed the $J \cong 15$ rotational transitions of XeO_3 with the K components resolved. The XeO_3 spectrum was taken at an elevated temperature of about 100°, and the concentration of XeO_3 vapor was estimated to be not more than a few per cent.

In summary, in the bond-stretching region, distinct infrared bands are observed and there are more than one would expect for O_h symmetry. In the bond-stretching region, however, no definite absorption bands can be located. Further, no microwave absorption could be detected in the range 3.7–8.6 cm^{-1}.

These results seem to support either a model that is very nonrigid with respect to angles between bonds or a model of more rigidity but with unusually large anharmonicities in the bending potential function. The anharmonicities are particularly important for such a molecule because of the many low-lying vibrational energy levels. Calculation of Boltzmann distributions, using rough estimates of 200 cm^{-1} for all three triply degenerated bending modes and 600 cm^{-1} for the stretching fundamentals, shows that less than 1% of the molecules at room temperature are in the vibrational ground state. There are 15 excited states for which the populations are comparable to that in the ground state. Thus the spectral features should broaden markedly owing to anharmonicities.

Our results, on the other hand, do not give any support to Bartell's inverting or pseudo-rotator model.[9] Since the results are negative, they cannot definitely rule it out. When the inverting model is taken to parallel that of a rotating diatomic molecule with $B = 3$ cm^{-1} as suggested, an upper limit to the magnitude of the transition dipole moment can be set. Assuming the same values for the vibrational fundamentals as above except the f_{1u} bending mode which transforms to the pseudo-rotation mode, the calculated value of the upper limit[14] is about 0.1 D.

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[13] R. Kewley, K. B. L. N. Sastry, M. Winnerwisser, and W. Gordy *J. Chem. Phys.*, **39**, 2856 (1963).

[14] For example, C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 24.

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Infrared Spectra of Copper Thiocyanate Complexes

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In metal ion compounds the linear thiocyanate ion can coordinate through either the sulfur or the nitrogen atoms, or both.[2] Examples of complexes containing each type of bonded thiocyanate group are known but in general the compounds with first-row transition metals are known to be N-bonded from X-ray data.[3,4] Criteria for establishing the mode of bonding in thiocyanate complexes have been worked out based on the frequency ranges found for the three vibrational modes of the thiocyanate ion, *i.e.*, the C–N[5] and C–S[6–8] stretching modes ν(CN) and ν

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[1] Ashland Chemical Co., Minneapolis, Minn. 55420

[2] S. E. Livingstone, *Quart Rev.* (London), **19**, 386 (1965).

[3] B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, **16**, 753 (1963).

[4] M. A. Porai-Koshits and G. N. Tishchenko, *Soviet Phys. Cryst.*, **4**, 216 (1959).

[5] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

[6] M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem Soc.*, **81**, 6412 (1959).

[7] A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

[8] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).