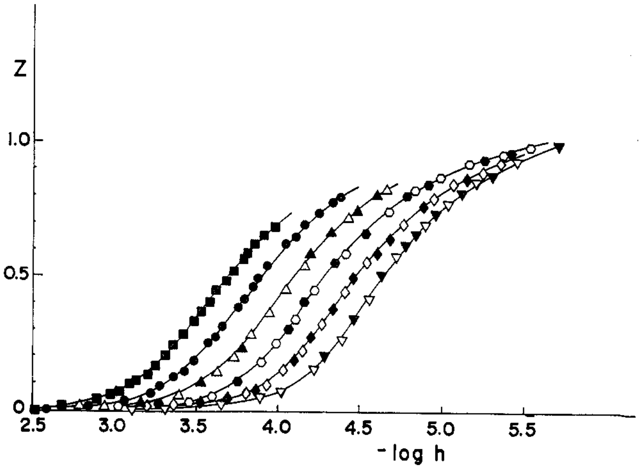

Figure 2.—Z as a function of $-\log h$ in the aqueous solution system. Symbols were the same as those in Figure 1. Curves were calculated with the values in Table I.

LiClO$_4$ medium in the present series of work was about 0.6 lower in the log $^*\beta$ unit than that reported by them in 3 M NaClO$_4$ medium. The change of the constant may be caused by the change of the medium salt.

The $Be_2(OH)_2^{2+}$ complex was found only in the system of the highest dioxane concentration studied. The presence of the species was thus not sure.

A slight decrease in the equilibrium constant of the formation of Be_2OH^{3+} was observed with an increasing concentration of dioxane in the solvent and an increase in the constant for $Be(OH)_2$ was found when the concentration of dioxane increased from 0.1 to 0.2 mole fraction. However, for such minor components the values of the equilibrium constants might be sensitive by a small uncertainty of the equilibrium constant of the main species and small experimental errors. Therefore, it seems reasonable to give a conclusion only for the main species: the equilibrium constant for the formation of $Be_3(OH)_3^{3+}$ is changed only to a very small extent with the solvent composition of dioxane–water mixtures.

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Raman Spectrum of Xenon Hexafluoride

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The structure of XeF_6 molecules has been the subject of a number of studies over a period of about 3 years. Because of experimental difficulties due to the reactivity of the material and because some of the properties of this molecule seem to be unique, the problem of structure continues to be a challenge.

Only incomplete infrared and Raman spectra have been reported. Smith[1] studied the infrared spectrum of the vapor from 400 to 1400 cm^{-1} and also reported an observation by George Begun of Raman bands for the solid at 655, 635, and 582 cm^{-1}. Hyman and Quarterman[2,3] observed Raman bands at 660, 620, and 600 cm^{-1} for XeF_6 dissolved in HF.

We have measured the Raman spectra of XeF_6 for the solid at $\sim$40°, for the liquid at 54 and 92°, and for the vapor at 94° and $\sim$2 atm pressure. A Spectra-Physics Model 125 laser was used as a source of $\sim$50 mw of exciting light at 6328 A. The exciting light was mechanically chopped at 400 cps. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim-50°$, and an ac lock-in amplifier. The samples were contained in a cell that was a nickel block suitably drilled and fitted with sapphire or CaF_2 windows and thin Teflon gaskets. A hole 2 mm in diameter is drilled all the way through the 1 × 2 × 2 in. nickel block. It is closed at the top by a sapphire window through which the laser beam could enter and at the bottom by a mirror. A 20-mm long section of the 2-mm hole is milled open in the central section and covered by a calcium fluoride window 30 mm in diameter to permit the scattered radiation to escape at right angles to the laser beam. The cell was designed for liquid samples, but was used also to study solid XeF_6 and to obtain preliminary results for the vapor.

The results of the study are shown in Figures 1–4. The traces of Figures 1 and 3 were obtained with the incident light polarized perpendicular to the line from sample to spectrophotometer slit. On Figures 2 and 4 traces are shown for both perpendicular and parallel polarizations of incident light. Polarization characteristics are indicated qualitatively in these figures rather than quantitatively because of the reflections from the cylindrical sample container. The frequencies given in the figures are, in most instances, average values obtained from several scans.

Figure 1 shows that definite changes in relative intensities and band shapes occur with changing temperature in the liquid. Comparison of Figures 2 and 3 shows a striking similarity between the spectra of the solid and of the lower temperature liquid. These observations indicate that the groups of four molecules whose xenon atoms are at corners of a tetrahedron in the solid[4] tend to persist in the liquid as polymers, probably tetramers. The band at 506 cm^{-1} increases by a factor of 3 to 5 in warming from 54 to 92° and is probably the only monomer band that is not overlapped by polymer bands. In the vapor, which is

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[1] D. F. Smith, "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 300.

[2] H. H. Hyman and L. A. Quarterman, ref 1, p 278.

[3] H. H. Hyman, *Science*, **145**, 3634 (1964).

[4] P. A. Agron, C. K. Johnson, and H. A. Levy, *Inorg. Nucl. Chem. Letters*, **1**, 145 (1965).

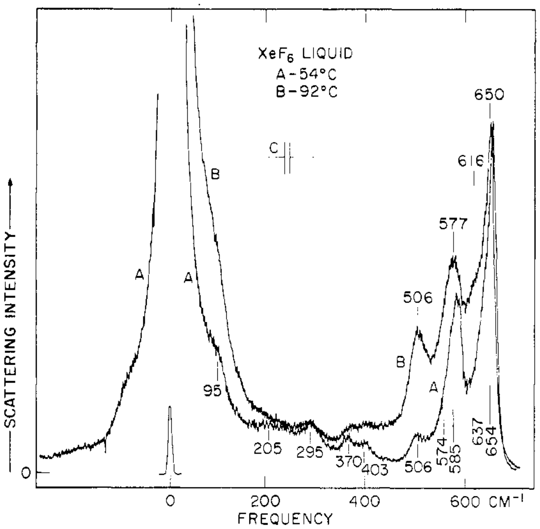

Figure 1.—Raman spectrum of liquid XeF_6: A, sample at 54°; B, sample at 92°; C, equivalent slit width.

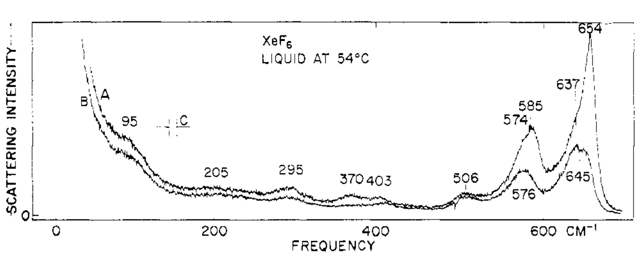

Figure 2.—Raman spectrum of liquid XeF_6 at 54°: A, incident polarization perpendicular; B, incident polarization parallel; C, equivalent slit width.

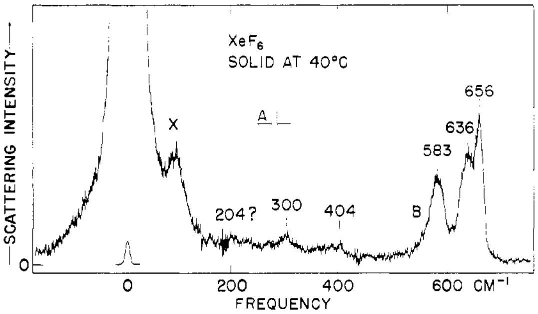

Figure 3.—Raman spectrum of solid XeF_6 at 40°.

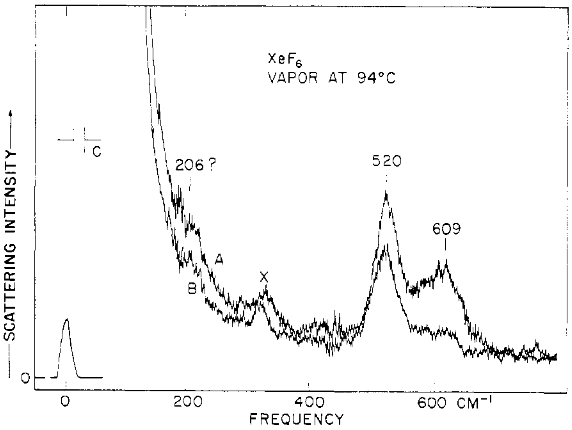

Figure 4 —Raman spectrum of XeF_6 vapor at 94°: A, incident polarization perpendicular; B, incident polarization parallel; C, equivalent slit width.

known to be essentially monomeric from vapor density measurements,[5] this band is shifted to 520 cm^{-1}.

Fifteen hexafluoride molecules had been studied before the preparation of XeF_6 and all had been found to have octahedral vapor molecules of symmetry O_h. Such molecules have three Raman-active fundamentals. They characteristically show up as a sharp, highly polarized band of highest frequency, a depolarized band 50–100 cm^{-1} lower, and a depolarized band of much lower frequency—assigned to species a_{1g}, e_g, and f_{2g}, respectively. The spectrum of XeF_6 vapor is similar to this pattern, but differs strikingly in that the highest frequency, polarized band is so broad. It is difficult to see how the "breathing" vibration of a symmetrical hexafluoride can show up in the Raman spectrum as anything but a sharp, line-like band.

The infrared spectrum of XeF_6 vapor shows two distinct absorption maxima in the bond-stretching region[1] at 613 and 520 cm^{-1}, whereas an O_h molecule has only one active stretching fundamental. Now it may be noted that there is a very close coincidence in frequency between infrared and Raman for both stretching bands.

These observations lead to the conclusion that either the ground-state vapor molecules possess a symmetry lower than O_h or they have some very unusual electronic properties that markedly influence the region of spectrum usually considered the vibrational–rotational region. Unfortunately, a more detailed conclusion cannot be given at the present time. The problem is one of unusual difficulty whose solution will require results from a wide variety of measurements, some of which have not yet been completed.

Acknowledgment.—We want to express appreciation to J. G. Malm, F. Schreiner, and D. W. Osborne for making available to us part of the sample of XeF_6 whose purity was indicated to be above 99.8% by melting temperature measurements.

[5] B. Weinstock, E. E. Weaver, and C. P. Knop, *Inorg. Chem.*, **5**, 2189 (1966).

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A New Synthesis of Chlorine Nitrate

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Previous methods for the preparation of chlorine nitrate involve the reaction of either Cl_2O or ClO_2 with NO_2 or N_2O_5.[1] To circumvent the use of these hazardous chlorine oxides, a new route to this compound was sought as indicated by the equation

$$ClF + HNO_3 \longrightarrow ClNO_3 + HF$$

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[1] (a) H. Martin, *Angew. Chem.*, **70**, 97 (1958); (b) M. Schmeisser, *Inorg. Syn.*, **9**, 127 (1967).