tion of ethers has been noted by many investigators.[16–18] A general correlation also appears to exist between the acceptor strength of the acid and the decrease in frequency.[16] Also, the decrease in C–N stretching frequencies of trimethylamine when it coordinates to boron halides has been noted by Amster and Taylor.[19]

It should be pointed out that previous investigators have presented discussions similar to the present one for individual ligands (*e.g.*, ref 14); however, to our knowledge a simple generalization which applies to a wide variety of ligands has not been presented before. Also, most discussions of intraligand stretch frequencies, for ligands which contain both σ and π bonds, concentrate exclusively on changes in the π bonds which occur upon coordination. The present results indicate that cognizance of changes in σ bonds may be in order.

Experimental Section

Spectra were recorded for Nujol mulls of the compounds on Beckman IR-11 and IR-12 instruments. The complexes were prepared according to published methods[20–21] and C, H, N, and Cl analyses were as good as or better than the original reports.

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The Nature of Aqueous Divalent Xenon[1]

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Aqueous solutions containing divalent xenon can be prepared by dissolving XeF_2 in water.[2] In the communication reporting this fact it was concluded that XeF_2 itself was the principal molecular entity present.[2] However, the presence of such species as XeF^+, Xe^{2+}, XeF(OH), and XeO was not entirely excluded. Appreciable formation of such species should impart measurable conductance to XeF_2 solutions, while if rapid equilibria are involved, even very slight formation of these species should bring about fluorine exchange between XeF_2 and aqueous fluoride.

This note reports measurements of the conductance of aqueous XeF_2 solutions and of the fluorine exchange between XeF_2 and aqueous HF and F^-.

Experimental Section

Xenon difluoride was prepared by heating a 10:1 mole mixture of xenon and fluorine overnight at 300° in a Monel container. The excess xenon was pumped off, and then about 10% of the product was distilled away to remove any XeF_4 that might have been formed. The final product was distilled under vacuum into a Kel-F tube, and water was added to make a saturated solution at 0°. The solution was analyzed by addition of sulfuric acid and sodium iodide and titration with standardized thiosulfate.[2] It was found to be 0.153 ± 0.0015 *M* in divalent xenon. The tube containing the solution was capped with a Kel-F stopper and stored in Dry Ice.

Mallinckrodt "Low-Sulfur" carbon tetrachloride was used in the exchange experiments. Other chemicals were commercial products of reagent grade. Distilled water was redistilled from alkaline permanganate or through hot copper oxide before use.

The conductance of a saturated XeF_2 solution at 0° was measured with a probe-type cell using shiny platinum electrodes and a 60-cycle ac bridge. Solid XeF_2 in a Kel-F tube was washed with several portions of 0° water and then dissolved as quickly as possible to make an approximately saturated solution for measurement. The conductances of HF solutions at 0° were also measured in Kel-F tubes. The conductance cell was calibrated with 1.00×10^{-3} *M* HCl at 25°. The specific conductance of this solution was taken to be 4.21×10^{-4} (ohm cm)$^{-1}$.[3]

Fluoride-containing solutions were analyzed by titration with thorium nitrate that had been standardized against sodium fluoride. The fluoride solution was first neutralized and then buffered with an equimolar mixture of chloroacetic acid and sodium chloroacetate. Sodium alizarin sulfonate was the indicator both for the neutralization and for the thorium titration.[4] If the fluoride solution contained XeF_2, it was first made alkaline to bring about rapid reduction of the XeF_2 by water, with formation of Xe, O_2, and F^-.[2] Titration with thorium then gave the total fluorine content of the solution.

Solutions containing radioactive fluorine-18 were counted in small tubes placed between two 3-in. sodium iodide scintillation crystals oriented face-to-face. The output of each crystal's photomultiplier tube was amplified and fed through a single-channel pulse height analyzer set to pass only pulses corresponding to the 510-kev annihilation radiation of F^{18}. The analyzer outputs went to a coincidence circuit that recorded only pulses coming simultaneously from the two analyzers. In this way the F^{18} annihilation radiation could be counted with high efficiency and very low background. Counting data were corrected for decay of the F^{18}.

To make HF^{18} for fluoride exchange measurements, a 3 *M* HF solution in a Kel-F tube was irradiated with neutrons and γ rays formed by electron bombardment of a tungsten target in Argonne National Laboratory's Linear Accelerator. This stock solution was used directly to make up reaction mixtures containing HF^{18} and XeF_2, and a portion of it was partially neutralized with KOH to make up reaction mixtures containing KF^{18}, HF^{18}, and XeF_2. The mixtures were made up in Kel-F tubes at 0°, and aliquots were counted and analyzed for total fluorine content. After standing for 2 hr at 0°, each mixture was transferred to a glass cylinder graduate and was shaken with about five times its

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2297 (1964).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p 537.

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volume of ice-cold CCl_4 to extract most of the XeF_2.[2] The aqueous phase was removed and the bulk of the CCl_4 was transferred to another vessel and centrifuged. An aliquot of the centrifuged CCl_4 was then shaken with aqueous 0.2 M NaOH to back-extract and decompose the XeF_2. This NaOH solution was counted, and its fluoride content was determined. Less than 0.004% of the total activity remained in the CCl_4 after back-extraction.

"Blank" experiments were carried out in the same way, but with no XeF_2 present. In such experiments less than 0.002% of the total activity was extracted into the CCl_4 and back-extracted with NaOH.

Results

A saturated XeF_2 solution at 0° was found to have a specific conductance of 4×10^{-4} (ohm cm)$^{-1}$. A 4.2×10^{-3} M solution of HF at 0° was found to have closely the same specific conductance.

Two reaction mixtures were typical of the fluorine exchange experiments. One contained 0.14 M XeF_2 and 0.33 M HF*; the other contained 0.13 M XeF_2, 0.13 M HF*, and 0.18 M KF*. In each of these experiments 25 ± 0.5% of the total fluorine was obtained by extracting the XeF_2 into CCl_4 and back-extracting it with base. In each case this fluorine contained 0.21 ± 0.01% of the total F^{18} activity. Thus after 2 hr at 0°, exchange had proceeded only to the extent of about 0.8%.

Discussion

The conductance found for a saturated XeF_2 solution is probably that of HF formed in the oxidation of water by XeF_2[2]

$$XeF_2 + H_2O \longrightarrow Xe + {}^1/_2O_2 + 2HF \qquad (1)$$

This reaction has a half-time at 0° of about 7 hr.[2] Among other reactions that might contribute to the condutance are

$$XeF_2 + H_2O \longrightarrow XeF(OH) + HF \qquad (2)$$

and

$$XeF_2 \longrightarrow XeF^+ + F^- \qquad (3)$$

If either of these reactions proceeded to the extent of about 3%, it could account for the entire observed conductance. Any other reaction one might write would have to produce at least as much conductance if it proceeded to the same extent. Hence, we can say, in any case, that at least 97% of the xenon difluoride dissolved in water is initially present in solution as molecular XeF_2.

The observed fluoride exchange between XeF_2 and aqueous fluoride is so slow that we may rule out the occurrence of any *reversible* reactions similar to reactions 2 and 3. We may also exclude such equilibria as

$$XeF_2 + 2F^- \rightleftarrows XeF_4^{2-} \qquad (4)$$

in which the fluorine atoms in the complex ion are equivalent.

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Correspondence

Force Constants for CO Bonds in Metal Carbonyls[1]

Sir:

There have been reported[2-6] a number of treatments of metal carbonyls in which the CO stretching force constants and CO,CO interaction constants have been calculated with neglect of all other force constants in the molecule. This gross approximation has apparently proved useful in making frequency assignments. However, little indication has been given as to how these "approximate" force constants may differ from the true harmonic force constants in a general quadratic valence force field.[7,8] For this reason it seems appropriate to compare the results obtained using the approximate method with those obtained using a more rigorous treatment for a given molecule. The hexacarbonyl of molybdenum is a well-studied example.

Recently[8] anharmonic corrections and harmonic frequencies were determined for the hexacarbonyls of Cr, Mo, and W. The harmonic frequencies are the appropriate values to use for force constant calculations, and the results calculated therefrom must be considered the most accurate. We shall compare the harmonic with the uncorrected results, as well as comparing the rigorous and "approximate" methods. The equations for the more rigorous treatment are in the literature.[9] For the approximate treatment[10] of octahedral $M(CO)_6$ these reduce to

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); (b) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(3) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(4) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *ibid.*, **3**, 1123 (1964).

(5) D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *ibid.*, **4**, 166 (1965).

(6) G. R. Van Hecke and W. D. Horrocks, Jr., *ibid.*, **5**, 1960 (1966).

(7) Van Hecke and Horrocks[6] did compare "approximate" calculations with "rigorous" calculations for $Co(NO)(CO)_3$, $Ni(CO)_4$, and $Mo(CO)_6$. However, harmonic frequencies (corrected for anharmonicity) were not available for the first molecule, and considerable revision[8] is necessary for the anharmonic corrections of the last two.

(8) J. M. Smith and L. H. Jones, *J. Mol. Spectry.*, **20**, 248 (1966).

(9) L. H. Jones, *ibid.*, **8**, 105 (1962).

(10) The approximate treatment referred to entails the neglect of all force constants but F_{CO}, $F_{CO,CO'}$, and $F_{CO,CO''}$; that is, $F_{MC,CO} = 0$, $F_{MC,CO'} = 0$, $F_{MC,CO''} = 0$, $F_{MC} = 0$, $F_{MC,MC'} = 0$, $F_{MC,MC''} = 0$, etc. Cotton and Kraihanzel[2] made the further approximation that $F_{CO,CO'} = 2F_{CO,CO''}$ This is not assumed here.