Infrared Spectra of Difluorophosphoric Acid[1]

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Abstract: The infrared spectra in the range 4000–400 cm^{-1} of liquid and of associated and monomeric gaseous difluorophosphoric acid, F_2POOH, are reported and assigned. The free OH stretch is at 3662/3678/3694 cm^{-1}. Using this, the strength of the hydrogen bonding is compared to that of other inorganic acids. The phosphoryl stretching frequency is compared to those of other gaseous XYZP=O compounds by means of a plot of frequency *vs.* average electronegativity. The OH group, as expected, acts much like a halogen with electronegativity of 3.4. Gaseous phosphorus monoxide, PO, also fits onto this plot. The corresponding vanadyl halides and vanadium monoxide, VO, are discussed.

Obtaining a phosphorus acid in the unassociated state has proved to be extremely difficult. The failure to observe the stretching vibration of a free –OH in very dilute solutions of phosphorus acids in nonpolar solvents led some workers to believe that the hydrogen bonding in phosphorus acids is intramolecular.[2,3] In a related situation, gaseous Cs_2SO_4 is reported to have V_d symmetry,[4] implying that each Cs is shared by two oxygens. $H_2SO_4(g)$, on the other hand, has each hydrogen attached to only one of the oxygens.[5] Thomas, *et al.*,[6] however, observed a band at 3600 cm^{-1} for ethyl methyl phosphonothionic acid in CCl_4 solution. In this compound the association would be between hydrogen and sulfur and so should be relatively very weak. The same authors used dilutions as high as *M*/35,000 for ethyl methyl phosphonic acid but failed to get any concrete evidence for the presence of free acid in the system. Peppard and co-workers[7] heated dilute solutions of phosphorus acids to temperatures as high as 160°, but failed to obtain any evidence of monomer formation. Their cryoscopic measurements[7,8] show that the monobasic acids are mostly dimerized and that the dibasic acids are mostly polymerized in solution. In acetic acid the acids appeared to be monomeric, but here it is a matter of solvent–solute interaction.

To use solutions of dilution as high as and higher than those used by Thomas, *et al.*,[6] would entail great technical problems in infrared spectroscopy. Another approach is to superheat and acid in the vapor state. Unfortunately phosphorus acids generally polymerize or decompose before they vaporize. One of the exceptions is difluorophosphoric acid, which boils at 116° at 760 mm.

To the best of our knowledge, there has been no report on the infrared spectra of difluorophosphoric acid in the literature. In this study we report the infrared spectra in the region 4000–400 cm^{-1} for the liquid acid and also of its vapor superheated up to 300°. The bands due to the associated and monomeric species are identified and assigned to the normal modes of vibration. A comparison of the strength of hydrogen bonding of this acid with those of some other inorganic acids also is made. Correlations of phosphoryl and vanadyl stretching frequencies are discussed.

Experimental Section

The apparatus used for the study of the vapor is described elsewhere.[5,9] Two kinds of cells were used: cell A for the study of the saturated vapor over the liquid acid and cell B for the study of the superheated vapor.

The spectra of the vapor were taken by the normal single-beam operation. All the precautions described in ref 5 and 9 were taken to prevent the acid vapors from reaching the windows. Extensive temperature cycling was used to identify any volatile impurities or decomposition products.

Because of the high volatility of the acid, the spectrum of the saturated vapor was too intense to be measured above 45°. For the superheated vapors, where the amount of the acid admitted into the cell could be easily controlled, the studies extended from room temperature up to a nominal temperature of 300°.

The spectrum of the liquid was taken by holding a thin film of the acid between AgCl plates. It was found that the acid was vaporized by the heat of the infrared light source. The spectrum was taken in the double-beam mode of operation.

Difluorophosphoric acid was a City Chemical Corp., New York, N. Y., product. To obtain pure spectra it was found necessary to distil the acid. The vapor at its boiling point attacked glass rather strongly.

Results and Discussion

On the basis of the known near-tetrahedral configuration of phosphoryl fluoride and other halides,[10] it is assumed that difluorophosphoric acid has an approximate tetrahedral configuration, and hence its skeleton should have Cs point symmetry. The skeleton has nine nondegenerate fundamental vibrations. Of these, four stretching bands are due to P–O, P–O(H), and PF_2 groups. PF_2 contributes also a bending and a rocking vibration: P=O and P–O(H), one wagging mode each. Finally, there is a torsion. In addition,

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[1] Supported principally by the U. S. Army Research Office, Durham, and in part by the Northwestern University Materials Research Center. Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 31, 1966, Abstract N131.

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[7] D. F. Peppard, J. R. Ferraro, and G. W. Mason, *J. Inorg. Nucl. Chem.*, 7, 231 (1958); **12**, 60 (1959).

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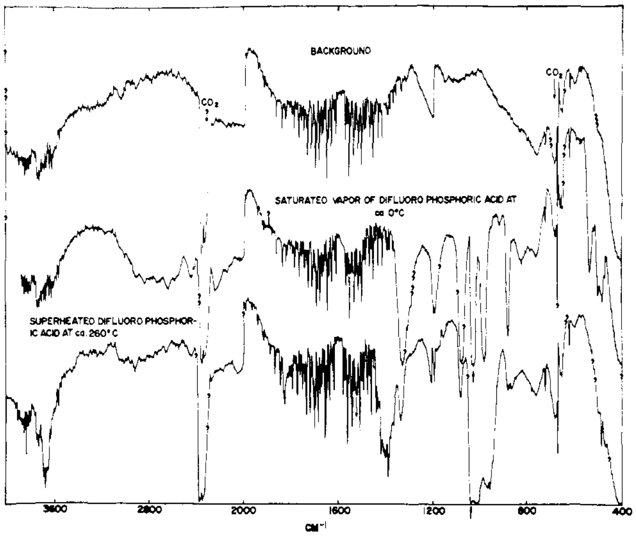

Figure 1. At top is the background. Breaks due to grating changes are at 670, 1200, and 2000 cm^{-1}. B (middle) is the spectrum of the vapor at 0°. C (bottom) is the spectrum of the vapor superheated to about 260°. The arrows indicate a band due to SiF_4 formed by attack of the glass cell.

the OH group contributes a stretching, a bending, and wagging mode.

In Figure 1, spectrum A is that of the background, spectrum B of the saturated vapor at about 0°, and spectrum C of the superheated vapor at about 260°. Table I summarizes the bands observed and gives their approximate description.

The broad band centered at about 2800 cm^{-1} is the -OH stretch of the associated species. Its position is at somewhat higher frequency than the -OH stretching frequencies of other phosphorus acids in the condensed phase. In spectrum C a new sharp band of medium strong intensity with PQR branches is seen at 3678 cm^{-1}. This is clearly due to the -OH stretching mode of the free molecule.

In Table II, the -OH stretching frequency of difluorophosphoric acid is compared with those of some other compounds. Difluorophosphoric acid has a very high -OH stretching frequency. This is expected,[11,12] because phosphorus has a low electronegativity and can release electrons to a bonding orbital in the O-H group.

In the same table, a comparison of the relative strength of hydrogen bonding, as indicated by the monomer-liquid frequency shift, is made. The fact that this shift in the -OH stretching frequency is greatest for difluorophosphoric acid indicates that it forms the strongest hydrogen bond. This inference is amply supported by the temperature dependence of the dissociation of the hydrogen-bonded species in the vapor state. The lower the electronegativity of the central atom, the more basic is the double bonded oxygen, which then forms stronger hydrogen bonds.

Rather weak, broad bands were observed at 2350 and 1650 cm^{-1}. The origin of these bands has been variously explained by other workers.[13,14]

Table I. Infrared Spectra of Difluorophosphoric Acid (cm^{-1})[a]

Liquid[b]	Vapor at *ca.* 0°	Superheated vapor at *ca.* 260°	Approximate description
		3694 3678 m 3662	-OH str (free) (a′)
2500–3000 w, b, max ≈ 2750	2500–3100 mb max ≈ 2800	2600–3100 w,b max ≈ 2850	-OH str (assoc)
2350 vw, b			Satellite band (?)
1660 w, b			Combination band (?)
		1393 ± 5 s	P=O st (free) (a′)
1335 s, b	1332 vs	1332 m	P=O st (assoc) (a′)
1219 m, b	1193 m	1193 m	P–O–H bend (assoc) (a′)
		1172 1181 w	P–O–H bend (free) (a′)
1070 m	1081 vs	1081 m	P–O(H) (assoc) (a′)
	1031 vvs	1031 vvs	SiF_4 str
		~1020	P–O(H) str (free) (a′)
978 s	983 s	983 m	PF_2 asym str (assoc) (a″)
		956 967 ms	PF_2 asym str (free) (a″)
888 ms	881 ms	881 ms	PF_2 sym str (assoc) (a′)
		865 873 m	PF_2 sym str (free) (a′)
	820 w		SiF_6(?)
545 m	535 m	535 vw	Impurity (or -OH wag (assoc) (a″))
490 ms	501 m	500 vw	PF_2 bend (a′)
	484 m	486 469	PF_2 rock (a″)

[a] w = weak, m = medium, s = strong, b = broad, v = very. [b] Many of the bands in the liquid are broad; frequency uncertainties of ±5 to ±10 cm^{-1} result.

Table II. -OH Stretching Frequencies (cm^{-1}) and Hydrogen Bonding

Compound	ν(OH) of the monomeric vapor	Shift in the -OH stretching frequency for the liquid–monomer vapor transition
NO_2–OH[a]	3550	140
ClO_3–OH[b]	3560	295
F-SO_2–OH[c]	3602	477
CH_3-SO_2–OH[d]	3610	633
F_2–PO–OH	3678	~900
CH_3–OH[e]	3682	...
OH[f]	3735	...

[a] G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, *J. Chem. Phys.*, **42**, 237 (1965). [b] P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962). [c] See ref 29. [d] See ref 9. [e] G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra," D. Van Nostrand, Inc., Princeton, N. J., 1945. [f] See ref 33.

The bands at 1335–1332 cm^{-1} for the liquid and the vapors are the P=O stretch of the associated molecule. The appearance of the band at 1393 cm^{-1} coincides with the appearance of the 3678-cm^{-1} band and is assigned to the P=O stretch of the free molecule.

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(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958.

(12) R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960).

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That there is a linear correlation between phosphoryl stretching frequency and the electronegativities of the substituent groups on the phosphorus atom is well recognized.[15–17] From this have emerged the terms "phosphoryl absorption shift constant"[15] and "π constants"[16] which are roughly equivalent to electronegativity. The phosphoryl absorption shift constant obtained by Bell and co-workers[15] for the -OH group is 2.3. This value is too small to be the electronegativity of the -OH group, which is expected to be between those of fluorine and chlorine. In order to check the above value, a plot of phosphoryl stretching frequencies of various compounds in the vapor state *vs.* the average electronegativity[18] of the substituents is made in Figure 2. In this, a phosphoryl stretching frequency of 1393 cm^{-1} would correspond as indicated by the arrow to an electronegativity of 3.4 for the $-OH$ group in difluorophosphoric acid. This is a reasonable value for the electronegativity of the -OH group and is the one used previously for the $X-SO_2-Y$ system.[5] It corroborates the assignment of the 1393-cm^{-1} band to the P=O stretch of the free acid. This behavior of OH as a pseudo-halogen has been used successfully also in the interpretation of electronic spectra,[19] and of bond energies and vaporization behavior.[20]

Though in the early work[21,22] the P-O-H bend in phosphorus acids was believed to be around 1030 cm^{-1}, in almost all recent work it is reported in the region of 1250 cm^{-1}.[6,23,24] Therefore, the broad band of medium intensity at 1219 cm^{-1} in spectrum A and the sharp band at 1193 cm^{-1} in spectra B and C are assigned to the P-O-H bend of the associated species. The weak doublet that appears at 1172/1181 in the high-temperature spectrum could be the P-O-H bend in the free state. This small shift to lower frequency is expected.[5,9,25]

It is in the region 1100-800 cm^{-1} that the P-O(H) and PF_2 stretches should be expected. There is no band in spectrum A that corresponds to the strong bands marked by arrows at 1031 cm^{-1} in spectra B and C. This is assigned to the stretch of SiF_4 which arises by attack of the cell material and increases consistently with time. The frequencies of the bands at 1070 and 1080 cm^{-1} in spectra A, B, and C are too high to be PF_2 stretches but are very close to what could be calculated for the P-O(H) stretch using the relation of Thomas and Chittenden,[14] namely, $\nu_{P-O-(H)} = 650 + 40\Sigma\pi$, where π is the "π constant" or roughly the electronegativity of the substituents on phosphorus. These bands are therefore assigned to the P-O(H) stretch of the associated species.

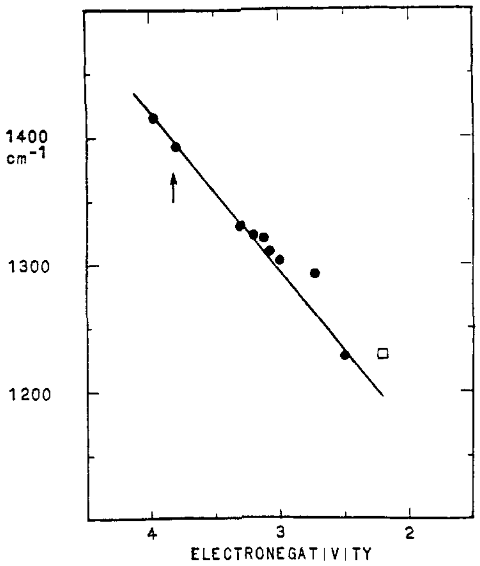

Figure 2. P=O stretching frequency (cm^{-1}) for gaseous XYZP=O *vs.* the average electronegativity of X, Y, and Z. The electronegativities are from Allred,[18] plus OH (3.4), CH_3 (2.5), and CH_3O (3.0). Starting at upper left, the points are for (1) phosphoryl fluoride,[26,27] (2) difluorophosphoric acid, (3) dimethyl phosphorofluoridate, (4) phosphoryl chloride, (5) methyl phosphorodichloridate, (6) dimethyl phosphorochloridate, (7) trimethyl phosphate, (8) dimethylphosphite, and (9) trimethylphosphine oxide (J. Goubeau and W. Berger, *Z. Anorg. Allgem. Chem.*, **304**, 147 (1960)). The line was drawn through points 1, 2, 4, 7, and 9. The other points were added later. Except as noted, all data are from unpublished work of this laboratory. The square is for the PO molecule (Herzberg) and is at the electronegativity of the P atom, 2.2.

The P-O(H) stretch of the free molecule should appear at lower frequency. This region, however, is obscured by the SiF_4 stretch. From a study of the contour of the SiF_4 band, it could be seen that a new band grows in at about 1020 cm^{-1}. This gives it a shift of about 60 cm^{-1} which is comparable to that for the P=O group. Such a comparison was observed also for the SO_2 and S-O(H) shifts in sulfuric and sulfonic acids.[5,9] However, when the various shifts for F_2POOH are added to Table VI of ref 5 [$\sim$900 (OH), 60 (P=O), -61 (P-O(H)], that for P-O(H) does seem small.

By comparison with the reported spectra for POF_3, POF_2Cl, and POF_2Br,[26–28] the asymmetric and symmetric stretches of the PF_2 group are assigned as shown in Table I. In the high-temperature spectrum, doublets appear at frequencies slightly lower than the above bands. These may be due to the corresponding bands of the free molecule. Such a shift to lower frequency was observed by us for the S-F stretch in fluorosulfonic acid.

The medium strong band for the liquid at 545 cm^{-1} and for the associated vapor at 535 cm^{-1} loses its intensity in the spectrum of the superheated vapor and so could be due to the -OH group. Since the -OH wag is known to be raised in frequency through hydrogen bonding,[29] these bands are possibly due to the -OH

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(16) L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, **20**, 407 (1964).

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wag of the associated species. This frequency is not as high as observed in H_2SO_4, indicating that they are more likely due to an impurity.

The last two bands are assigned to the PF_2 rocking and bending modes by analogy with the bands observed for POF_3, POF_2Cl, and $POBrF_2$.[26-28]

Figure 2 merits further discussion. It is justified in part by the assumption that the phosphoryl stretching frequency is free of mass and coupling effects;[30] in effect, this frequency is assumed to be factored out of the secular equation for the normal modes of vibration. The primary effect of the attached groups X in X_3PO may be considered, therefore, to be donation or withdrawal of electrons from the phosphoryl bond. In this approximation, gaseous phosphorus monoxide can be considered to have attached groups of the same electronegativity (2.2) as the P atom. This approximation is reasonable as shown by the square on Figure 2.

A theoretical explanation[31] of Figure 2 is that more electronegative substituents produce a net positive charge on the phosphorus. This in turn contracts the phosphorus 3d orbitals letting two of them accept electrons from the oxygen forming $p\pi$–$d\pi$ bonds. Vanadium, on the other hand, has d orbitals readily accessible, so that the corresponding shifts in the vanadyl stretching frequency are expected to be small. The data[28,32-34] are given in Table III. In agreement with the theory, the shifts are small.

Table III. M=O Frequencies (cm^{-1}) in X_3MO

X	P	V
F	1418[a]	1058[a]
Cl	1325[a]	1035[b]
Br	1261[a]	1025[b]
CH_3	1225[c]	
Monoxide	1231[d]	1012[e]

[a] See table given by Selig and Claassen[27] or ref 32. [b] Reference 32. [c] See caption to Figure 2, Goubeau and Berger. [d] Reference 33. [e] Reference 34.

In addition the monoxide frequencies[33] are shown. There is some question[34,35] about the assignment of the ground state for VO. By analogy with the phosphorus compounds, the vibration frequency 1012 cm^{-1} is reasonable.

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The H_0 Values of Aqueous Selenic Acid and Their Relationship with Aqueous Vapor Pressure[1]

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Contribution from the Chemistry Department of the University of Cincinnati, Cincinnati, Ohio 45221. *Received June 10, 1966*

Abstract: The H_0 values of aqueous selenic acid have been obtained using a series of primary aniline indicators over the concentration range of 2.8 to 85.7 wt % acid. The H_0 values obtained fall on the curve of H_0 *vs.* water activity previously established for the sulfuric acid and perchloric acid systems.

During the past dozen years there has emerged a growing awareness of an interrelationship between the Hammett acidity function, H_0, and the water activity of aqueous solutions of mineral acids.[2-11]

A major breakthrough in this area was the observation by Wyatt[4] that for aqueous solutions of sulfuric, perchloric, hydrochloric, and nitric acids the H_0 values were identical at the same water activity. Independdently, the same observation was made by Braun,[12] who pointed out that a plot of H_0 *vs.* the logarithm of the partial pressure of water for these same acid solutiins is single valued and continuous. He noted that the region between $H_0 = -5.0$ and -8.4 was established by a single acid, sulfuric acid. In order to better establish the relationship in this area, he determined the H_0 values and aqueous vapor pressure of several particular acid solutions, including 85.4% selenic acid using anthraquinone as an indicator.

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