

Vibrational spectra, assignments and normal coordinate analysis for difluorophosphine

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Abstract—Infrared spectra of the gas and Raman spectra of the liquid and solid forms of PF_2H and PF_2D are reported. A normal coordinate analysis based on compliance constants has been carried out on the assigned fundamentals and also on harmonic frequencies estimated by DENNISON's method.

INTRODUCTION

Difluorophosphine, PF_2H , was first reported and characterized relatively recently by RUDOLPH and PARRY [1]. They reported i.r. frequencies of the gas and solid, suggested tentative assignments and pointed out the marked effect which temperature and physical state had on the stretching frequencies. In particular, they noted that the P—H vibration shifted to a higher value upon going from the gas at room temperature to the solid at about -190° . Results based on studies in argon matrices [2] suggest that strong intermolecular interactions of the dipole-dipole type may exist in the solid, a conclusion which is further substantiated by other physical properties of the substance in condensed phases such as the Trouton constant, NMR chemical shifts, etc. [1] Microwave data [3] show that the molecule is an asymmetric top with a pyramidal structure, the F—P—F and F—P—H angles, respectively, being reported as 99.0° and 96.3° . Despite the simplicity of the molecule, vibrational assignments are not yet completely certain. No Raman results have been reported because of the tendency of the compound to undergo photodecomposition under normal conditions of excitation.

In the present work, Raman spectra of the liquid and solid have been obtained of the normal and deuterated species and i.r. spectra of the two species have been reexamined in the gaseous state. Assignments have been revised and a normal coordinate analysis has been carried out utilizing compliance constants. Harmonic frequencies estimated by means of DENNISON's method have also been subjected to a normal coordinate analysis.

EXPERIMENTAL

Difluorophosphine and deuterio-difluorophosphine were prepared as outlined in the literature [1] by the reaction of the appropriate phosphine with difluoroiodophosphine in the presence of mercury. The product was purified by careful trap-to-trap distillation on the vacuum

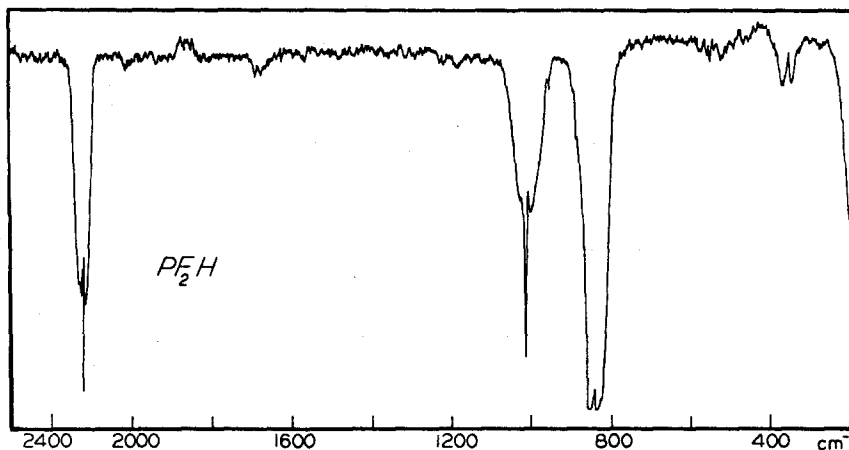
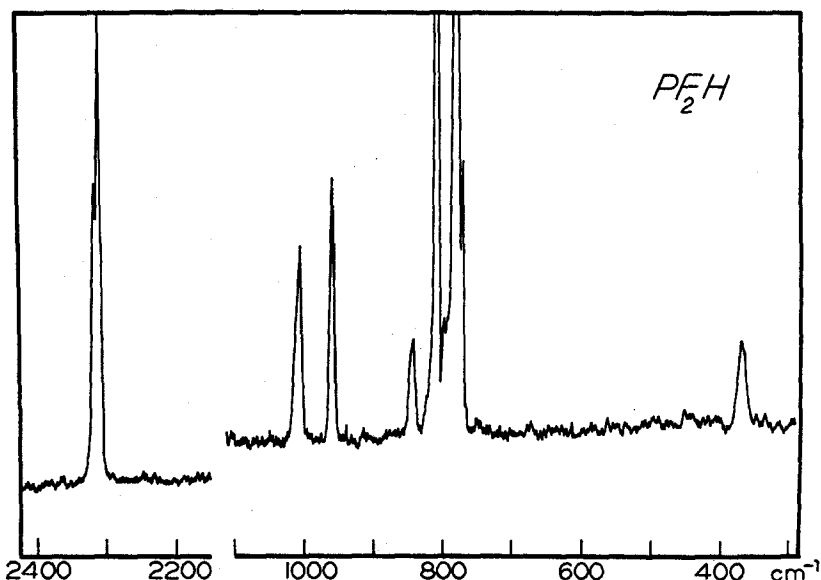
line and stored at liquid nitrogen temperatures until use. Vapor pressure and other physical properties agreed with those reported in the literature. Inasmuch as PF_3 has bands which interfere with those of PF_2H , particular attention was given in the purification procedures to the removal of PF_3 .

Since fluorophosphine compounds are very sensitive to impurities, particularly small traces of water, extreme care was taken to keep the vacuum line clean and to dry scrupulously cells and sample containers. Decomposition, when it occurred, could be detected by the formation of a thin yellow film on the container walls which scattered light strongly.

Infrared spectra were obtained using a Beckman IR-12 recording spectrometer which covered the range from 200 to 4000 cm^{-1} . Calibration of the spectrometer with the usual reference substances showed the instrument to be accurate within specifications. The gas spectra were obtained with a standard 10 cm path length cell with O-ring seals to CsI windows. Solid phase low temperature spectra were obtained using the low temperature cell described by FARRAN [4]. Raman spectra were recorded with a Spex 1401 Ramalog spectrometer using either the 6328 \AA line of a He—Ne laser or the 4880 \AA line of an argon ion laser as the source of exciting radiation. It was found that the photodecomposition reaction was greatly retarded at low temperatures if the samples had been carefully purified. Consequently, the purified compounds were condensed into 1 mm diameter capillaries which had been extensively flamed under vacuum prior to use and which were sealed off after partial filling. For spectral examination, the capillaries were inserted into a vacuum jacketed glass tube of approximately 25 mm outside diameter through which cold nitrogen gas was passing. The temperature of the samples was monitored by a copper-constantan thermocouple and controlled to within $\pm 5^\circ$ by adjusting the flow of nitrogen gas. Raman spectra of the solid and liquid phases, including polarization measurements for the latter, were obtained. Estimated uncertainties in frequencies are approximately 1 cm^{-1} .

EXPERIMENTAL RESULTS AND ASSIGNMENTS

The i.r. spectrum of gaseous PF_2H is shown in Fig. 1 and the Raman spectrum of the solid is displayed in Fig. 2. Experimental frequencies for PF_2H are tabulated in Table 1 and those for the deuterated species are given in Table 2. The molecule has six fundamental frequencies, four totally symmetric (a') and two asymmetric to the

Fig. 1. Infrared spectrum of gaseous PF_2H .Fig. 2. Raman spectrum of solid PF_2H at -150°C .

plane of symmetry (a''). All frequencies are active in both i.r. and Raman spectra and the normal modes can be described to a good approximation in terms of simple bond stretching and bending motions. The two points of uncertainty with respect to assignments involve the a' and a'' H—P—F deformations and P—F stretches. RUDOLPH and PARRY [1] observed two maxima at 1016 and 1008 cm^{-1} which they assigned respectively to the a' and a'' H—P—F deformations. However, the Raman spectra show there is only one fundamental in this vicinity but that there is a strong depolarized band at 960 cm^{-1} which has a very weak counterpart in the i.r. This must be the asymmetric deformation, ν_3 . The three i.r. maxima at 1008, 1016 and 1030 cm^{-1} are therefore assigned to P , Q , and R branches of ν_2 . Upon deuteration, the two deformation frequencies shift to 706 and

762 cm^{-1} , respectively, the a'' deformation remaining quite weak in the i.r. All deformation modes appeared relatively insensitive to temperature and phase.

For the P—F stretching frequencies, RUDOLPH and PARRY [1] assigned the a' and a'' modes, respectively, to bands at 851 and 838 cm^{-1} . However, as can be seen in Fig. 1, the bands in this region are quite intense, the two fundamentals overlap strongly and assignments are not immediately apparent. In the case of PF_3 , it appears well established [5, 6] that the symmetric (a_1) mode occurs at a higher frequency than the degenerate (e) mode. Furthermore, the e mode in PF_3 is somewhat more sensitive to change in state than the a_1 mode, the shift from gas to solid at -180° being 50 cm^{-1} ; the shift of the a_1 band is 35 cm^{-1} [6, 7]. We believe that the a' and a'' P—F

Table 1. Observed i.r. and Raman frequencies of PF₂H

	Infrared Gas (25°C)	Raman		Assignment
		Liquid (-80°C)	Solid (-150°C)	
			92 w 159 w	Lattice mode Lattice mode
P R	347 367 } m	363 w, p	374 w	ν_4
			773 m, sh	?
P Q R	826 839 852 } vvs, br		783 vvs	ν_6
			800 m, sh	?
P R	826 852 } vvs, br	811 m, br	810 vs	ν_3
			845 m	?
	959 vvw	960 m, dp	960 m	ν_5
P Q R	1008 1016 1030 } s	1013 ms, p	1008 ms	ν_2
P Q R	2228 2242 2257 } s	2261 s, p	2311 vs	ν_1
			2318 m, sh	

Notation used: s = strong; m = medium; w = weak; v = very; sh = shoulder; br = broad; p = polarized; dp = depolarized.

Table 2. Observed i.r. and Raman frequencies of PF₂D

	Infrared Gas (25°C)	Raman		Assignments
		Liquid (-80°C)	Solid (-150°C)	
			98 w 158 w	Lattice mode Lattice mode
P R	348 365 } m	360 w, p	373 w	ν_4
	701 vw	703 m, dp	706 m	ν_5
	720 vvw			$2\nu_4$
	768 ms	763 ms, p	762 ms	ν_2
	813 vvw, sh			?
P Q R	828 839 853 } vvs, br		788 m, sh	ν_6
P R	828 853 } vvs, br	808 m, br	819 vvs	ν_3
	893 w			PF ₃ impurity
	1100 vvw			Impurity
	1605 vvw			$\nu_2 + \nu_3$
P Q R	1625 1643 1652 } s	1655 s, p	1683 vs	ν_1
			1688 m, sh	?

stretching frequencies are accidentally degenerate in the gas spectrum but shift by different amounts on going to the solid spectrum, the two shifts being 29 and 56 cm⁻¹. In the Raman spectrum of the liquid, the separation is not complete and the two bands overlap. However, the highly frequency side of the composite band clearly was polarized which, together with the assumption that the shifts are similar to those of PF₃, provides evidence that the 810 cm⁻¹ band of the solid is the *a'* mode and the 783 cm⁻¹ band is the *a''* mode.

The P—F stretching region in the Raman spectrum of the solid was unexpectedly complex and exhibited three distinct maxima in addition to the two fundamentals. No satisfactory explanation for this complexity is apparent although the P—F bonds seem to be particularly sensitive to the known strong intermolecular forces. In this respect it is of interest to note that even in an argon matrix, P—F fundamentals not attributed to aggregate species were reported to be split [2].

As was reported previously, the position of the

P—H stretch was found to be markedly affected by temperature and phase although this region was not complex as was the P—F stretching region. The maximum of the P—H stretch shifted approximately 70 cm^{-1} to higher frequency in the solid compared to the gas, a direction which is opposite to that usually found when hydrogen bonding is present. Apparently, this type of interaction in the solid does not exist. The revised

assignments of the fundamentals are listed in Table 4. For the A' class, the theoretical Teller-Redlich product rule ratio is 1.860 which can be compared with the experimental value of 1.812; corresponding values for the A'' class are 1.376 and 1.367, respectively.

VIBRATIONAL ANALYSIS AND DISCUSSION

Symmetry coordinates and the corresponding numbering scheme for the fundamentals are listed in Table 3. Harmonic frequencies were estimated by DENNISON's method [9] assuming that the anharmonicity coefficient, x_{ij} , is the same for all frequencies of a given class. The correction for anharmonicity in the j th frequency is thus given by $\Delta\nu_j^i = x_{ij}\omega_j \approx x_{ij}\nu_j$ where the index, i , refers to the symmetry class. The harmonic frequencies so derived are listed in Table 4.

Table 3. Symmetry coordinates for PF_2H

A' Class		
$S_1 = \Delta d$		P—H stretch
$S_2 = 2^{-1/2}(\Delta\alpha_1 + \Delta\alpha_2)$		HPF deformation
$S_3 = 2^{-1/2}(\Delta r_1 + \Delta r_2)$		P—F stretch
$S_4 = \Delta\beta$		PF_2 deformation
A'' Class		
$S_5 = 2^{-1/2}(\Delta\alpha_1 - \Delta\alpha_2)$		HPF deformation
$S_6 = 2^{-1/2}(\Delta r_1 - \Delta r_2)$		P—F stretch

Table 4. Observed fundamentals and estimated harmonic frequencies for PF_2H and PF_2D , and differences from calculated values (in cm^{-1})

	PF_2H				PF_2D			
	ν_i	Δ	ω_i	Δ	ν_i	Δ	ω_i	Δ
ν_1	2242	-16.5	2398	1.1	1642	11.4	1727	-0.8
ν_2	1016.5	-7.1	1049	-0.5	768	5.0	784	0.3
ν_3	839	-0.2	860	-0.1	839	-0.3	860	0.1
ν_4	357	0.3	360.5	0.0	356	-0.3	360	0.0
ν_5	959	-3.2	979.2	0.0	701.5	2.1	711.7	0.0
ν_6	839	0.0	854.4	0.0	839	0.0	854.4	0.0

$\Delta = \text{Experimental} - \text{calculated}$.

Table 5. Symmetry and valence force and compliance constants for PF_2H

Index	Observed frequencies		Harmonic frequencies	
	Compliance constants	Force constants	Compliance constants	Force constants
Symmetry constants				
1, 1	0.354	2.891	0.309	3.275
2, 2	0.765	1.356	0.730	1.403
3, 3	0.200	5.077	0.190	5.323
4, 4	0.790	1.265	0.775	1.290
5, 5	1.156	0.882	1.116	0.915
6, 6	0.217	4.699	0.209	4.881
1, 2	0.078	-0.301	0.051	-0.230
1, 3	—	-0.073	—	-0.050
2, 3	-0.048	0.328	-0.042	0.308
5, 6	0.072	-0.284	0.070	-0.307
Valence constants				
r (P—F)	0.209	4.888	0.200	5.102
d (P—H)	0.354	2.891	0.354	3.275
α (H—P—F)	0.961	1.119	0.923	1.159
β (F—P—F)	0.790	1.265	0.775	1.290
rr	-0.009	0.189	-0.010	0.221
$r\alpha$	0.012	0.022	0.014	0.001
$r\alpha'$	-0.060	0.306	-0.056	0.308
$d\alpha$	0.055	-0.213	0.036	-0.163
$\alpha\alpha$	-0.196	0.237	-0.193	0.244

Units: stretch = $\text{mdyn}/\text{\AA}$; stretch-bend = mdyn ; bend = $\text{mdyn}\cdot\text{\AA}$.

Table 6. Thermodynamic properties of PF₂H

T °K	C _p /R	(H° - H ₀ °)/ RT	-(G° - G ₀ °)/ RT	S/R
273.15	5.536	4.504	26.821	31.325
298.15	5.775	4.600	27.219	31.820
300	5.792	4.608	27.248	31.856
350	6.243	4.810	27.973	32.783
400	6.645	5.014	28.629	33.643
450	6.997	5.216	29.231	34.447
500	7.302	5.409	29.791	35.200
550	7.567	5.594	30.315	35.909
600	7.797	5.768	30.809	36.577
650	7.999	5.932	31.278	37.210
700	8.177	6.086	31.723	37.810
750	8.334	6.231	32.148	38.379
800	8.473	6.367	32.554	38.921
850	8.597	6.494	32.944	39.438
900	8.707	6.614	33.319	39.933
950	8.806	6.727	33.679	40.406
1000	8.895	6.833	34.027	40.860

The normal coordinate analysis was carried out using a standard iterative least squares program to fit both experimental and harmonic frequencies with a potential function expressed in terms of compliance constants. Computational details have been described previously [8]. G matrix elements were evaluated using molecular parameters from the microwave work [3]. Only three off-diagonal constants appeared significant in the refinement, two in the *a'* class and one in the *a''* class. The remaining off-diagonal constants were constrained to zero on the basis of exploratory calculations which indicated their magnitude was likely to be quite small. The analysis confirmed the simple description of the normal modes since the potential energy distribution showed virtually no mixing of coordinates. Differences between observed and calculated frequencies are given in Table 4. Symmetry compliance constants and the corresponding force constants obtained by inversion of the compliance matrices are tabulated in Table 5; the derived valence force and compliance constants are given in the same table.

DUNCAN and MILLS [10] have determined reliable values for the force constants of PH₃ based on isotopic data and coriolis constants. Their P—H valence stretching force constant (harmonic) is 3.45 mdyn/Å which is not significantly different

from the value of 3.28 mdyn/Å in Table 5. The corresponding values for *f_{PH}* based on experimental (anharmonic) frequencies are 2.97 mdyn/Å for PH₃ [10] and 2.89 mdyn/Å from Table 5. Although coriolis data were not available in the present work, the closeness of these numbers suggests that the P—H bond is very similar in PH₃ and PF₂H.

Force constant data in the literature for PF₃ [6, 11–13] are not entirely consistent and no "best" value seems available for the P—F bond. In the most recent study by CLARK and RIPON [6], a value of 4.7 mdyn/Å for the combination (*f_r* - *f_{rr}*) was obtained; this is very close to the value for *F₆₆* in Table 5 which represents the same combination. Other comparisons indicate that the P—F bonds in PF₂H are quite similar to those in PF₃ and the net conclusion is that the properties of the intermediate molecule represent a logical interpolation from those of the two binary compounds.

Thermodynamic properties based on observed fundamentals and the usual rigid rotor-harmonic oscillator approximation are given in Table 6.

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