Vibrational Spectra and Thermodynamic Properties of Difluoroiodophosphine

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Raman and infrared spectra in the range 20—1200 cm^{-1} have been measured for PF_2I. Vibrational assignments are made on the basis of these spectra and of approximate normal co-ordinate calculations; statistical thermodynamic functions have been calculated. Statistical thermodynamic functions for PF_3 have been calculated using revised data.

IN a previous report[1] on the gas-phase i.r. spectrum of PF_2I above 200 cm^{-1} assignments were made for four of the six fundamental frequencies; estimates of the remaining two vibrational frequencies have also been made[2a] in order to compute statistical thermodynamic functions and subsequently force constants,[2b] and mean amplitudes of vibration.[2c] In the present work, liquid- and solid-state Raman spectra and gas-phase i.r. spectra over the range 20—1200 cm^{-1}, and the solid-phase i.r. spectrum over the range 375—1200 cm^{-1}, were recorded. Assignments have been made for all six fundamental frequencies, and used to compute statistical thermodynamic functions. Some disagreement over the assignments for the fundamental vibrational frequencies of PF_3, and the resulting statistical thermodynamic functions has arisen.[3,4] These have therefore been recalculated using very recently published geometrical data for PF_3[5] and further vibrational measurements.

EXPERIMENTAL

Preparation of PF_2I.—PF_2I was prepared as outlined by Parry *et al.*[1] using diethyl- rather than dimethyl-aminodifluorophosphine in order to facilitate the separation of PF_2I from unchanged starting material. The diethylaminodifluorophosphine was prepared in a manner similar to that described by Schmützler,[6] using continuous removal of product by distillation.

PF_2I, free of HI impurity, was obtained by mixing impure PF_2I with P_2F_4, followed by high-vacuum trap-to-trap distillation to remove PF_2H and residual P_2F_4. Although the PF_2I only momentarily came into contact with vacuum grease on removing the gas from the reaction vessel, it was found that initial use of Silicone High Vacuum Grease (Edwards High Vacuum Ltd.) caused an unexplained i.r. band to appear at 1140 cm^{-1}. In all subsequent preparations this was avoided by using Kel-F Grease (Minnesota Mining and Manufacturing Company).

Infrared Spectra.—The range 1200—375 cm^{-1} was covered using a Unicam SP 100 spectrometer with PF_2I

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[1] R. W. Rudolph, J. G. Morse, and R. W. Parry, *Inorg. Chem.*, 1966, **5**, 1464.

[2] (*a*) A. Müller, E. Niecke, B. Krebs, and O. Glemser, *Z. Naturforsch.*, 1968, **23b**, 588; (*b*) A. Müller, B. Krebs, I. Elvebredd, B. Vizi, and S. J. Cyvin, *J. Mol. Struct.*, 1968, **2**, 149; (*c*) I. Elvebredd, B. Vizi, S. J. Cyvin, A. Müller, and B. Krebs, *ibid.*, p. 158.

[3] M. K. Wilson and S. R. Polo, *J. Chem. Phys.*, 1952, **20**, 1716.

[4] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, 1952, **20**, 1652.

[5] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, 1969, **8**, 867.

[6] R. Schmützler, *Inorg. Chem.*, 1964, **3**, 415.

contained in a 10-cm path-length cell at pressures of *ca.* 13 hN m^{-2} (10 mmHg). The region 420—190 cm^{-1} was examined on a far-infrared grating spectrometer constructed in the Department, using a 10-cm path-cell with polyethylene windows at PF_2I pressures of 40—70 hN m^{-2} (30—50 mmHg). The range 220—20 cm^{-1} was covered using a Grubb–Parsons N.P.L. 'Cube' interferometer adapted to take a 110-cm path-length gas cell with polyethylene windows; pressures of PF_2I between 40 and 130 hN m^{-2} (30 and 100 mmHg) were employed. Solid-state i.r. spectra (between 375 and 1200 cm^{-1}) were obtained by spraying gaseous PF_2I on to a liquid-nitrogen-cooled CsI plate *in vacuo*.

Raman Spectra.—Solid-state Raman spectra were obtained using a simple evacuated low-temperature cell in which a jet of gaseous PF_2I was allowed to impinge on a spot cooled by liquid nitrogen: the spot was then rotated and the cell placed in the sample compartment of a Cary 81 Raman spectrometer to detect 180° scattered radiation. A Spectra-Physics He–Ne laser (632·8 nm ≡ 6328 Å) was used for excitation. The liquid-phase spectrum was obtained by allowing PF_2I to melt while sealed in a capillary tube.

Calculations.—In the absence of published structural data for PF_2I it was necessary to make certain assumptions about the molecular geometry in order to carry out both the normal co-ordinate analysis and the computation of the statistical thermodynamic functions. The structural parameters for PF_2I were estimated by comparison with PF_3,[5] PI_3,[7a] and P_2I_4 [7b] taking P–I = 247 pm (2·47 Å) and $\widehat{IPI} = 100{\cdot}0°$. The values used in the calculation were obtained by using the P–F bond length = 157·0 pm (1·570 Å) and $\widehat{FPF} = 97{\cdot}8°$ from PF_3 and the P–I bond length above. $\widehat{IPF}$ (99°) Was taken as the mean of $\widehat{FPF}$ in PF_3 and $\widehat{IPI}$ in PI_3. The estimated limits of error in the bond lengths are ±5 pm (±0·05 Å) and in the angles ±2°. For the calculations of thermodynamic functions for PF_3 the recent electron diffraction data of Morino *et al.*[5] was used.

(i) *Normal co-ordinate calculations.* The object of these calculations was not to attempt to evaluate a force field but rather to employ a 'reasonable' set of constants transferred from the parent PF_3 and PI_3 [8] molecules in order to calculate an approximate set of vibrational frequencies and normal co-ordinates which could assist in the assignment of the observed frequencies. Hence no great effort was made to force a fit between experimental and observed frequencies, although several small adjustments were made from the preliminary choice in order to produce a reasonable match. The force constants finally adopted are listed in Table 2. These values are similar to those used by Müller *et al.*[2b] with the exception of the P–I stretching force constant (f_{P-I}). For this a value of 130 N m^{-1} was used in the present calculations compared to 250 N m^{-1} employed by Müller *et al.*

The **B** matrix elements were computed directly from a set of cartesian co-ordinates for the molecule. Subsequently solution for the eigenvalues and eigenvectors of $(\mathbf{BM}^{-\frac{1}{2}})^t\mathbf{F}(\mathbf{BM}^{-\frac{1}{2}})$ was obtained (where $\mathbf{F}$ is the force constant matrix for the internal co-ordinates and $\mathbf{M}^{-\frac{1}{2}}$ is the diagonal matrix with the non-zero entries equal to the square roots of the reciprocals of the atomic masses). The set of frequencies calculated using the above force field is shown in Table 3 together with the approximate potential-energy distribution among the internal co-ordinates for each mode. Observed gas-phase frequencies are also shown for comparison.

TABLE 1

Infrared and Raman spectra of difluoroiodophosphine

Infrared (cm^{-1})		Raman (cm^{-1})	
(Gas)	(Solid)	(Solid)	(Liquid) [a]
851s	821·5s	862m	873w
846s	806vs	807m	
418m			
413m	397·5m	398m	408m
408m			
381m			
375m		378s	372m
369m			
208w			
202·5w		207vs	204·5m
197·5w		201m	

[a] After removal of PI_3 bands.[9] s, strong; m, medium; w, weak; v, very.

TABLE 2

Force constants utilised in normal co-ordinate calculations

Stretching [a]		Bending [a]	
PI	130	FPI	40
PF	490	FPF	65
PI/PF	10	FPI/FPI	3
PF/PF	30	FPI/FPF	3

[a] Units of N m^{-1}.

TABLE 3

Observed and calculated gas-phase infrared frequencies (cm^{-1})

Observed	Calculated	Species	Potential-energy distribution
851	859	*a′*	93% PF str.
846	833	*a″*	99% PF str.
413	401	*a′*	93% FPF def.
375	382	*a′*	46% PI str., 53% FPI def.
204	209	*a″*	99% FPI def.
198	181	*a′*	55% PI str., 43% FPI def.

(ii) *Thermodynamic functions.* Using the ideal-gas harmonic oscillator approximation and the above geometrical assumptions together with the observed gas-phase i.r. fundamental frequencies (see Table 3), rotational and vibrational contributions to the total statistical thermodynamic functions for PF_2I were calculated.

For PF_3 the fundamental vibrational frequencies are listed as 892(*e*), 860(a_1), 487(a_1), and 344(*e*) cm^{-1} by Wilson and Polo;[3] Gutowsky and Liehr,[4] however, assign a band at 532 cm^{-1} rather than that at 344 cm^{-1} as the *e* class fundamental. In this work no evidence was found in the gas-phase i.r. spectrum of PF_3 for the 532 cm^{-1} band; all other frequencies were in agreement with those of Polo and Wilson. Accordingly these latter were adopted in the calculations.

By varying bond lengths, bond angles, and vibrational frequencies within the experimental limits given above for PF_2I and repeating the calculations with the adjusted data, the maximum percentage errors over the temperature range considered were found to be ±0·3% for $C_p°$, ±0·2% for

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[7] 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' The Chemical Society, London, (*a*) *Special Publ.* No. 11, 1958; (*b*) *Special Publ.* No. 18, **1965**.

[8] T. R. Manley and D. A. Williams, *Spectrochim. Acta*, **1965**, **21**, 1773.

$(H_T^\circ - H_0^\circ)/T$, $\pm 0{\cdot}4\%$ for $-(G_T^\circ - H_0^\circ)/T$, and $\pm 0{\cdot}4\%$ for S°.

RESULTS AND DISCUSSION

Vibrational Spectra of PF_2I.—For an assumed C_s symmetry, six fundamentals ($4a' + 2a''$) are expected, both species being active in the i.r. and Raman. The observed spectra are shown below in Figures 1 and 2, with the bands listed in Table 1. The gas-phase frequencies in the i.r. region are in good agreement with those of Rudolph *et al.*[1] for the region above 250 cm^{-1}. Two fundamental modes (a' and a'') are expected below this but only one region of absorption (centred at *ca.* 203 cm^{-1}) could be detected in the i.r. spectrum; similarly only one Raman emission below 250 cm^{-1} was initially seen, which appeared as a strong asymmetric band in the solid-state spectrum at 208 cm^{-1}. An attempt to obtain a liquid-state Raman spectrum at room temperature was made in order to obtain polarisation data but it was apparent that the laser beam had caused considerable decomposition to PI_3, with characteristic strong bands [9] at 330, 306, and 113 cm^{-1} being observed, as well as the PF_2I bands. On the basis of the approximate normal co-ordinate calculations these low-frequency modes were predicted to lie at *ca.* 181(a') and 209(a'') cm^{-1}. In the absence of i.r. absorption or Raman shifts below 200 cm^{-1} it seems likely that both of these fundamentals must be located in the region of 200 cm^{-1}. The i.r. absorption is complex (see Figure 1) and could well consist of two overlapping bands. Under higher resolution there are clearly two bands (at 208 and 201 cm^{-1}) in the solid-state Raman spectrum. We have accordingly assigned the more intense Raman band to the symmetric mode and the weaker band to the a'' mode. The strong i.r. bands centred at 413 and 375 cm^{-1} both have the same overall shape and are assigned by Rudolph *et al.*[1] as FPF symmetric deformation and PI stretching modes respectively. The solid-state Raman spectrum has bands at 395w and 377s cm^{-1} which are identified with these modes. The calculations yield a' bands at 401 and 383 cm^{-1} in agreement with this assignment, the 382 cm^{-1} mode being considerably mixed in character (see Table 3). The large contribution from the P–I stretch in this mode may qualitatively account for the greater intensity relative to the higher frequency mode. The bands at 851 and 846 cm^{-1} are strong in the i.r. region and weak in the Raman and are certainly the P–F stretching modes. The higher-frequency band at 862 cm^{-1} in the solid-state Raman spectrum is considerably the more intense of the two, suggesting that it is the symmetric (a') mode, in agreement with the assignment of Rudolph *et al.*[1] This assignment is supported by the calculations which also indicate that the modes are almost pure P–F stretches. The bands at 83, 66, and 56 cm^{-1} observed in the solid-state Raman spectrum are presumably associated with lattice vibrations.

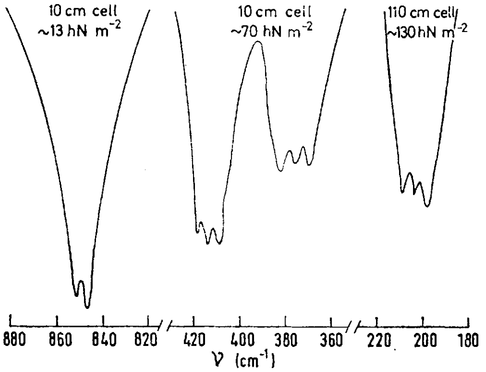

FIGURE 1 Gas-phase i.r. spectrum of PF_2I

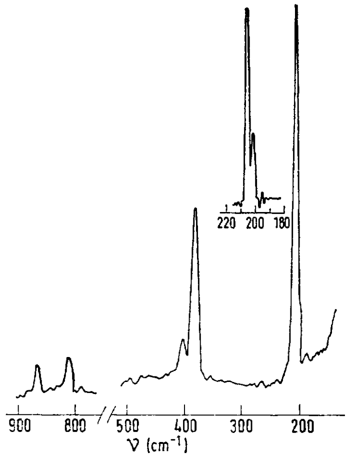

FIGURE 2 Solid-phase Raman spectrum of PF_2I

TABLE 4

Computed thermodynamic functions for difluoroiodophosphine—perfect gas at 101·325 kN m^{-2} (1 atm)

Product of the 3 principal moments of inertia = $3{\cdot}884885 \times 10^{-113}$ g^3 cm^6

T/K	C_p° (cal mol^{-1} deg^{-1})	$(H_T^\circ - H_0^\circ)/T$ (cal mol^{-1} deg^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (cal mol^{-1} deg^{-1}	S° (cal mol^{-1} deg^{-1})
100·00	10·468	8·704	52·779	61·483
179·60 [a]	13·212	10·138	58·258	68·396
200·00	13·748	10·480	59·367	69·846
273·15	15·311	11·576	62·800	74·376
298·15	15·739	11·907	63·828	75·735
299·85 [b]	15·766	11·929	63·896	75·825
300·00	15·769	11·931	63·902	75·833
400·00	17·052	13·063	67·496	80·559
500·00	17·861	13·948	70·510	84·458
600·00	18·384	14·647	73·117	87·764
700·00	18·734	15·207	75·419	90·626
800·00	18·977	15·664	77·480	93·144
900·00	19·151	16·042	79·348	95·390
1000·00	19·280	16·360	81·055	97·415

[a] M.p.[1] B.p.[1] (1 cal = 4·1868 J).

Thermodynamic Functions.—Computed statistical thermodynamic functions for PF_2I are presented in Table 4. These may be compared with those of Müller *et al.*[2a] which were computed using estimated values (190 and 170 cm^{-1}) for the two lowest frequency fundamentals and on the basis of P–F = 155 pm (1·55 Å). The maximum percentage deviations of their results

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[9] S. G. Frankiss, F. A. Miller, H. Stammreich, and T. T. Sans, *Spectrochim. Acta*, 1967, **23***A*, 543.

from the present work caused by differences in fundamental frequencies employed are 0·815% in $C_p°$, 1·622% in $(H_T° - H_0°)/T$, 0·452% in $-(G_T° - H_0°)/T$, and 0·524% in $S°$.

Calculated thermodynamic functions for PF_3 agree substantially with those of Müller *et al.*[2a] (although different structural data were employed) but differ considerably from those of Nagarajan.[10] Nagarajan used the frequencies given by Gutowsky and Liehr[4] and the geometry given by Sheridan *et al.*[11] [P–F = 153·5 pm (1·535 Å) and $\widehat{FPF}$ = 100°]. The maximum deviations of Nagarajan's results amount to 6·8% in $C_p°$, 6·8% in $(H_T° - H_0°)/T$, 2·6% in $-(G_T° - H_0°)/T$, and 2·6% in $S°$. Using available thermodynamic data, the standard free-energy for the decomposition reaction of PF_2I:[1]

$$3PF_2I_{(g)} \longrightarrow 2PF_{3(g)} + PI_{3(c)} \Delta G° = -21 \text{kJ} \ (-5{\cdot}0 \text{ kcal})$$

has been calculated[12] taking the bond energies in $PF_2I_{(g)}$ as equal to the mean bond dissociation energies in $PF_{3(g)}$ and $PI_{3(g)}$.

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[2/052 *Received, 11th January*, 1972]

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[10] G. Nagarajan, *Ind. J. Pure Appl. Physics*, 1964, **2**, 237.

[11] Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, 1952, **20**, 164.

[12] C. R. S. Dean, Ph.D. Thesis, London University, 1972.