

Vibrational spectra and assignments for $(\text{CH}_3)_2\text{NPF}_2$

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Abstract—Infrared and Raman spectra of dimethylaminodifluorophosphine have been obtained for the gaseous and liquid states at room temperature and for the solid at low temperature. Vibrational assignments are proposed based on a C_s model.

DIMETHYLAMINODIFLUOROPHOSPHINE is representative of a class of compounds generically related to trifluorophosphine through the replacement of one or more fluorine atoms by amine residues. These substances behave as Lewis bases and exhibit basicities intermediate between those of simple ethers and free amines [1–3]. Coordination compounds of these ligands and transition metals have been described recently [2] as well as complexes with typical Lewis acids [1, 3]. In the case of dimethylaminodifluorophosphine, evidence has been supplied [1] that coordination may occur either through the nitrogen or phosphorous atom, depending on the nature of the Lewis acid.

No spectroscopic study of $(\text{CH}_3)_2\text{NPF}_2$ has been published although its principal infrared bands have been reported [2, 3]; infrared frequencies and qualitative assignments for the chlorine analog have appeared [4]. In the present investigation, infrared spectra of the compound in the gaseous and solid states and Raman spectra of the liquid and solid have been obtained and assignments are proposed.

EXPERIMENTAL

Dimethylaminodifluorophosphine—This compound was prepared by the direct reaction of dimethylamine and trifluorophosphine under controlled conditions in the vacuum line and given an initial purification by fractionation. This was followed by a second distillation from anhydrous CoBr_2 which freed it from traces of $(\text{CH}_3)_2\text{NH}$ and bisdimethylaminofluorophosphine. The purified material melted at -87°C and had a vapor pressure of 93.4 mm at 0°C . Further characterization of the compound including analytical data, molecular weight and other physical and chemical properties is given in detail elsewhere [1]. Since the compound is decomposed by moisture and contact with strong bases, cells, containers and apparatus with which it came in contact were acidified and then carefully dried to prevent decomposition.

Spectroscopy—For the Raman spectra of the liquid, the material was condensed into capillary cells which were then sealed off. Unless special precautions were taken to eliminate water, the samples developed a slight turbidity or deposited a light sediment after a few hours making it difficult to obtain an intense spectrum free of background. The spectrograph and light source used have been described

[1] SISTER M. A. FLEMING, G. KODAMA and R. W. PARRY, to be published.

[2] R. SCHMUTZLER, *Inorg. Chem.* **3**, 415 (1964).

[3] R. C. CAVELL, *J. Chem. Soc.* 1992 (1964).

[4] R. B. HARVEY and J. E. MAYHOOD, *Can. J. Chem.* **33**, 1552 (1955).

previously [5]. Solid Raman spectra at approximately -160°C were obtained using an arrangement employing multilayer interference filters patterned somewhat after that described by SCHRADER [6]. More complete details will be given elsewhere. Frequency measurements were made both on the plates and on tracings, the data listed representing averages from several samples. The estimated probable error of most bands is 2 cm^{-1} with somewhat larger values for weak bands. Qualitative polarization measurements were made using the two exposure method and polaroid cylinders.

The infrared instruments were Perkin-Elmer Model 21 spectrophotometers equipped with NaCl, CaF_2 or KBr prisms and calibrated periodically with an indene standard. A standard 10 cm cell was used for the gas work while the spectra of the solid films at liquid nitrogen temperatures were obtained in a familiar T-shaped cell by depositing the vapor directly on a KBr window in good thermal contact with a copper block attached to a liquid nitrogen reservoir. Estimated probable errors in the frequencies are of the order of 2 or 3 cm^{-1} below 2000 cm^{-1} and of the order of 5 to 8 cm^{-1} above.

EXPERIMENTAL RESULTS

The observed infrared and Raman frequencies under the various conditions are tabulated in Table 1 together with approximate intensities, depolarization information

Table 1. Infrared and Raman spectra of $(\text{CH}_3)_2\text{NPF}_2$

gas	Infrared		Raman		Assignment
	solid (-190°)	liquid (-30°)	solid (-160°)		
2925 m	3002 vw	2998 s, sh, dp	2996 s	ν_{17}, ν_{18}	
	2932 mw	2945 vs, dp	2935 vs	ν_{19}	
2865 sh		2912 vs, p?	2906 vs, sh	ν_1	
		2861 s, p	2867 s	ν_2	
2820 w	2817 vw	2814 s, p	2815 s	ν_3	
	1498 w			$728 + 764 = 1492$	
1507	1490 m	1487 m, dp	1495 m	ν_{20}	
	1473 w			$707 + 764 = 1471$	
	1463 w			$393 + 1073 = 1466$	
1432 w	1455 m			ν_{21}	
	1443 w	1439 s, dp	1432 s	ν_{22}	
	1430 vw			$707 + 728 = 1435$	
1307 m		1414 w, sh, dp?		ν_4, ν_5	
	1313 s	1306 m, p	1315 m	ν_6 sym. CH_3 deform.	
	1233 vw			$499 + 728 = 1227$	
1195 m	1206 m			$\nu_{23}?$	
	1191 s			$\nu_{25}(\nu_7, \nu_{23}?)$	
1073 w	1145 vw			asym. C—N stretch	
		1103 vw	1107 m	ν_8 or ν_{24} CH_3 rock	
	1073 m	1071 w, dp?	1075 m	ν_8 or ν_{24} CH_3 rock	
	1002 sh			$\nu_7, \nu_{23}(\nu_{25}?)$ CH_3 rock	
989 s	994 s	989 m, dp?	999 m	$2 \times 499 = 998$	
814 s	764 s	792 m, p?	759 m	ν_9 sym. C_2NP stretch	
770 s	728 m	743 m, dp?		ν_{26} asym. P—F stretch	
704 m	707 vs	705 vs, p	704 s	ν_{10} sym. P—F stretch	
501 w, br	499 w	495 m	494 w	ν_{11} sym. N—P— F_2 stretch	
	486 vvw			ν_{12} sym. PF_2 deform.	
		393 w		skeletal?	
		336 m		ν_{13} sym. NC_2 deform.	
		239 w		ν_{14} sym. NC_2 rock	
		173 w		ν_{15} or $\nu_{25}?$	
		97 vvw		ν_{16} or $\nu_{28}?$	
				$\nu_{30}?$	

[5] G. L. VIDALE and R. C. TAYLOR, *J. Am. Chem. Soc.* **78**, 294 (1956).

[6] B. SCHRADER, F. NERDL, and G. KRESZE, *Z. Phys. Chem., N. F.*, **12**, 132 (1957).

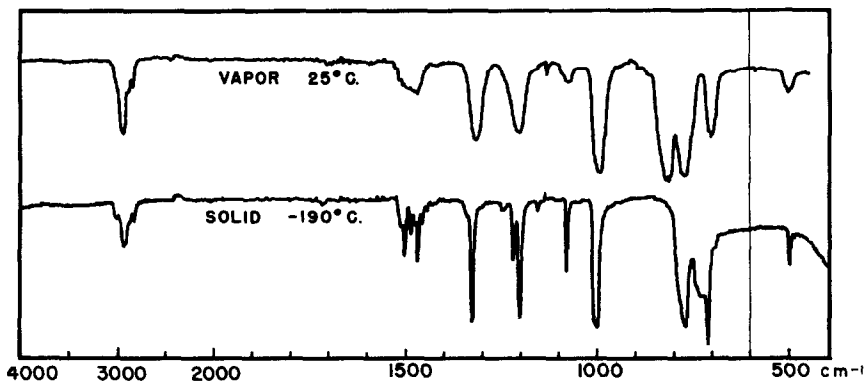


Fig. 1. Infrared Spectra of $(\text{CH}_3)_2\text{NPF}_2$.

and assignments. Figure 1 shows typical infrared spectra of dimethylaminodifluorophosphine in the vapor state at room temperature and as a solid at -190°C . The Raman spectrum of the liquid at -70°C is shown as a microphotometer tracing in Fig. 2.

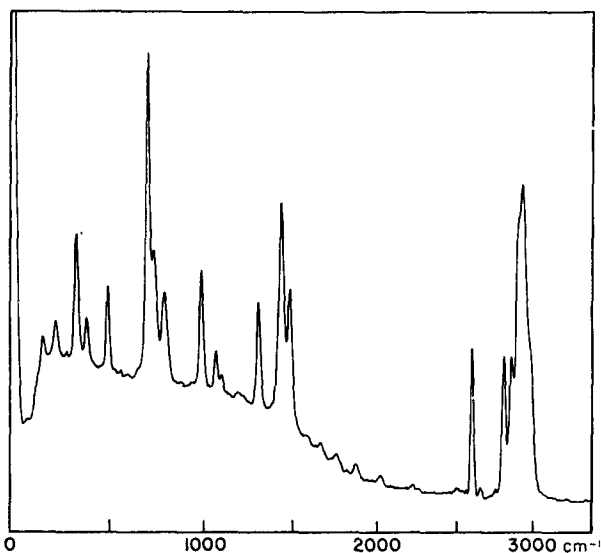


Fig. 2. Raman Spectrum of Liquid $(\text{CH}_3)_2\text{NPF}_2$ at -70° .

RESULTS AND DISCUSSION

No structural data for this molecule have been published but chemical reasoning argues that the pyramidal arrangement of bonds around both the nitrogen and phosphorus found in $(\text{CH}_3)_3\text{N}$ and PF_3 is retained.* However, the relative orientation

* Indirect evidence favoring a non-planar structure for the C_2NPF_2 skeleton has been obtained from the spectrum of the Lewis complex of $(\text{CH}_3)_2\text{NPF}_2$ with BH_3 . The frequencies of the free base are shifted relatively little in the complex, an observation consistent with a pyramidal arrangement around the phosphorus, the site of bonding. If the free base were planar, complexing undoubtedly would distort it into a non-planar configuration and a much more marked spectral difference would result than is observed. Results for Lewis complexes of $(\text{CH}_3)_2\text{NPF}_2$ will be reported separately.

of the two ends of the molecule with respect to each other cannot be decided with any certainty. Clearly, the *cis* configuration appears least favored for steric reasons but no satisfactory choice can be made between the *gauche* (hydrazine-like) structure and the completely *trans* arrangement. The possibility of a labile equilibrium existing between the latter two forms appears eliminated by the spectra. Figure 1 shows the infrared spectra of the gas and of the solid at low temperatures. The presence of rotational isomers in equilibrium usually is revealed by the simplification of the spectra in the transition from the gas or liquid to the solid. In the present case, no significant change occurs, other than the normal increase in line sharpness, indicating an appreciable barrier to internal rotation around the P—N bond.

Somewhat arbitrarily, the *trans* model having C_s symmetry has been assumed for purposes of classification in the present work. The thirty normal vibrations of the molecule under this point group divide into sixteen A' and fourteen A'' modes. A qualitative description and the numbering system is given in Table 2. For simplicity in discussion, the fundamentals may be divided into two groups, one containing

Table 2. A description of the fundamental vibrations of $(\text{CH}_3)_2\text{NPF}_2$

A' Symmetry		A' Symmetry	
Number	Notation	Number	Notation
1	$\nu^a\text{C—H}$	17	$\nu^a\text{C—H}$
2	$\nu^s\text{C—H}$	18	$\nu^s\text{C—H}$
3	$\nu^s\text{C—H}$	19	$\nu^s\text{C—H}$
4	$\delta^a\text{CH}_3$	20	$\delta^a\text{CH}_3$
5	$\delta^s\text{CH}_3$	21	$\delta^s\text{CH}_3$
6	$\delta^s\text{CH}_3$	22	$\delta^s\text{CH}_3$
7	ρCH_3	23	ρCH_3
8	ρCH_3	24	ρCH_3
9	$\nu\text{C}_2\text{—N—P}$	25	$\nu^a\text{C—N}$
10	$\nu^s\text{P—F}$	26	$\nu^s\text{P—F}$
11	$\nu\text{N—P—F}_2$	27	$\omega\text{N}(\text{CH}_3)_2$
12	δPF_2	28	τCH_3
13	$\delta\text{N}(\text{CH}_3)_2$	29	ωPF_2
14	$\rho\text{N}(\text{CH}_3)_2$	30	τPN
15	τCH_3		
16	ρPF_2		

ν = Stretching Mode

τ = Torsional Mode

δ = Deformation Mode

ω = Wagging Mode

ρ = Rocking Mode

s = Symmetric

a = Asymmetric

(for methyl group motions, the designation s and a refers to the local C_{3v} of the methyl group)

frequencies primarily associated with the methyl groups and the other with motions of the molecular skeleton. With one exception, no particular discussion of the methyl frequencies appears useful since they appear in the normal regions of the spectrum. Any assignments would to a large degree be arbitrary and subject to revision since considerable overlapping is present. The presence of a band at 2820 cm^{-1} , however, is worth comment. SHEPPARD *et al.* [7], in a study of sixteen compounds containing the $=\text{N}(\text{CH}_3)$ group, observed that all contained a band in the $2760\text{--}2820\text{ cm}^{-1}$ region. This band, which presumably is a symmetric C—H stretch, was further correlated by them with the presence of an unshared electron

[7] J. T. BRAUNHOLTZ, E. EBSWORTH, F. MANN and N. SHEPPARD, *J. Chem. Soc.* 2780 (1958).

pair on the nitrogen since it disappeared upon salt formation or upon coordination of the nitrogen. The 2820 cm^{-1} band in the present case exhibited the same behavior and the usefulness of this observation for diagnostic purposes is accordingly extended.

The six-atom skeleton of dimethylaminodifluorophosphine should provide seven A' and five A'' frequencies all lying below about 1200 cm^{-1} . These fundamentals are characteristic of the molecule and their correct assignment is important for the interpretation of the spectra of complexes in which $(\text{CH}_3)_2\text{NPF}_2$ acts as a base. Related molecules whose assignments are pertinent to the present work include dimethylamine [8], trimethylamine [8, 9], trifluorophosphine [10, 11] and dimethylaminodichlorophosphine [4].

The intense infrared bands at 814 and 770 cm^{-1} in the spectrum of the gas clearly are the two P—F stretching modes. Polarization data from the Raman effect indicate that the lower is the symmetric mode although the uncertainty associated with the measurement was higher than desirable for a clear choice. It is of interest to note that the position of these two bands shifted markedly and systematically to lower frequency in the transitions from gas to liquid to solid. None of the other frequencies showed an effect of the same magnitude, the shifts for the others at most being a few cm^{-1} as compared to about 50 cm^{-1} for the bands in question. Since the stretching frequencies of PF_3 also show a marked shift to lower frequency in the transition from gas to liquid [12], a strong intermolecular interaction involving the P—F bands must be present in the liquid state of these compounds.

The two other A' skeletal stretching modes can be described superficially as symmetric C—N and P—N stretches. The former is best identified with a band at 989 cm^{-1} despite the fact that its polarization state in the Raman effect is uncertain and it is significantly higher than the assigned symmetric C—N mode in both di- and trimethylamine. BELLAMY [13] considers a band in this region to be characteristic of the $(\text{CH}_3)_2\text{NP}$ -group and its failure to agree more closely with the corresponding amine frequencies probably is due to the normal coordinate containing an appreciable admixture of the P—N stretch. Attempts to identify a characteristic P—N stretching frequency in other molecules [13] have not been particularly successful, probably because it couples readily with other skeletal motions. Values in the region between 680 – 750 cm^{-1} have been suggested. The most intense Raman band (polarized) of $(\text{CH}_3)_2\text{NPF}_2$ falls at 705 cm^{-1} and probably involves a principal contribution from the P—N stretching although clearly being a mixed mode. It is tentatively described as a symmetric NPF_2 stretch.

The two A' scissors motions of the NC_2 and PF_2 end groups are assigned from a comparison with the symmetric deformation frequencies of $(\text{CH}_3)_3\text{N}$ and PF_3 . The remaining two A' skeletal modes involving rocking motions of the same two end

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- [8] J. R. BARCELO and J. BELLANATO, *Spectrochim. Acta* **8**, 27 (1956).
[9] E. J. ROSENBAUM, D. J. RUBIN and C. R. SANDBERG, *J. Chem. Phys.* **8**, 366 (1940).
[10] R. C. TAYLOR and T. C. BISSOT, *J. Chem. Phys.* **25**, 780 (1956).
[11] M. K. WILSON and S. R. POLO, *J. Chem. Phys.* **20**, 1716 (1952).
[12] R. C. TAYLOR, unpublished Raman data.
[13] BELLAMY, *The Infrared Spectra of Complex Molecules* (2nd ed.), p. 323, Wiley (1958).

groups are not assigned due to lack of information; they probably are included among the low frequency Raman lines observed.

Of the A'' skeletal modes, the asymmetric PF_2 stretch has already been mentioned. The other asymmetric stretching mode involving the NC_2 end group must lie in the region between 1000 and 1250 cm^{-1} but an unequivocal choice is difficult because of the presence of CH_3 rocking modes in this region. The assignments of BARCELO [5] for free di- and trimethylamine place the asymmetric C—N stretch for both molecules between 1025 and 1050 cm^{-1} . However, STEWART [14], from a study of

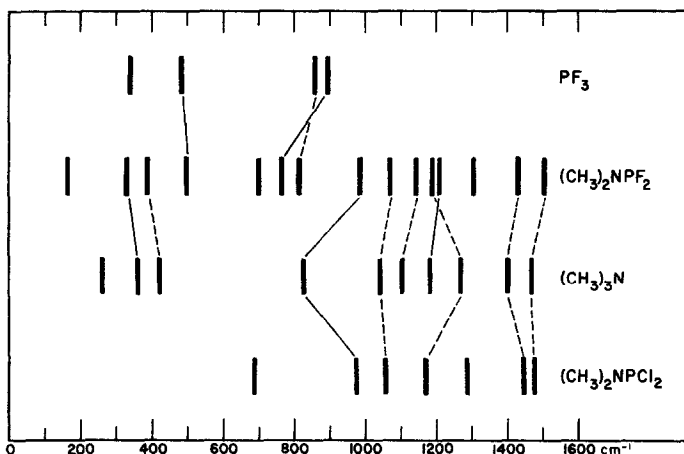


Fig. 3. Comparison of vibrational frequencies of $(\text{CH}_3)_2\text{NPF}_2$ and related compounds (in cm^{-1}). ——— Symmetric modes, - - - - Asymmetric modes.

some thirty primary and secondary amines, assigns the asymmetric NC_2 stretch to the region between 1140 and 1180 cm^{-1} . Although a clear decision between the two choices cannot be made without spectra from the deuterated species and possibly a normal coordinate treatment, the higher value agrees better with data from analogous hydrocarbons and is given preference here. The remaining A'' skeletal modes involve wagging motions of the end groups and the torsional vibration around the P—N axis. These fundamentals undoubtedly are low in frequency and no secure basis exists at present for their assignment. The bar graph shown in Fig. 3 portrays the relationship of the frequencies of dimethylaminodifluorophosphine to those of trifluorophosphine, trimethylamine and the chloro compound.

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[14] J. E. STEWART, *J. Chem. Phys.* **30**, 1259 (1959).