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## Comment on the »Calculation of the Thermodynamic Functions of Tetrafluorodiphosphine«

Vladimir Petruševski

*Institute of Chemistry, Faculty of Science, Arhimedova 5, 91000 Skopje, Yugoslavia*

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In a recent note,<sup>1</sup> the thermodynamic functions of tetrafluorodiphosphine (P<sub>2</sub>F<sub>4</sub>) were calculated, employing the ideal-gas rigid-rotor harmonic-oscillator approximation. Several points concerning the assignment of the bands in the vibrational spectra, the calculation of the thermodynamic functions and the stability of the compound are discussed.

In a recent paper, Nešković<sup>1</sup> calculated the thermodynamic functions of P<sub>2</sub>F<sub>4</sub>. However, it seems that important facts have been disregarded, thus making the calculation less accurate and highly speculative.

1) Most values for  $C_{P,m}^{\circ}$  given in Table I,<sup>1</sup> could not be reproduced with the given set of spectroscopic data and, therefore, appear to be misprinted (or miscalculated). The differences in the values of the other thermodynamic functions are within 0.5%  $R$  and result, most probably, from the differences in the adopted values of the physical constants.

2) The author has, probably, overlooked the paper by Rhee *et al.*<sup>2</sup> in which the authors claimed that »*The substance is stable as long as it is kept frozen at low temperature, but when the vapour is warmed to room temperature it slowly decomposes to give PF<sub>3</sub> as a yellow residue*«. Keeping this in mind, one can hardly find any real use of the values of the thermodynamic functions calculated up to 1000 K! If, on the other hand, the compound was thermally stable, the free rotation around the P-P bond would become very important as the temperature is raised (the rotational barrier was estimated<sup>3</sup> to be within 4–10.4 kJ · mol<sup>-1</sup>), thus making the employed model unsuitable.

3) It is not clear whether the calculated thermodynamic functions are related to the enthalpy of dissociation. Furthermore, no mention is made (although it was indicated in the abstract) of the equilibrium constant for the reaction of dissociation:  $P_2F_4 \rightleftharpoons 2PF_2$ .

TABLE I

*Frequencies, symmetry species and assignments of the P<sub>2</sub>F<sub>4</sub> normal modes*

Mod no.	$\nu/\text{cm}^{-1}$	Species	Assignment	Ref
1	825	$A_g$	PF <sub>2</sub> stretch	4
2	541	$A_g$	PP stretch	4
3	377	$A_g$	PF <sub>2</sub> wag	4
4	214	$A_g$	PF <sub>2</sub> scissors	4
5	843	$A_u$	PF <sub>2</sub> stretch	4
6	514	$A_u$	PF <sub>2</sub> rock	2
7	103	$A_u$	PF <sub>2</sub> twist	2
8	803	$B_g$	PF <sub>2</sub> stretch	4
9	453	$B_g$	PF <sub>2</sub> rock	4
10	831	$B_u$	PF <sub>2</sub> stretch	4
11	365	$B_u$	PF <sub>2</sub> wag	4
12	202	$B_u$	PF <sub>2</sub> scissors	2

4) The frequencies of the normal modes were taken from the paper of Rudolph *et al.*<sup>4</sup> It should be noted that the Raman data are for a liquid P<sub>2</sub>F<sub>4</sub> sample and the IR data are for a gas! The complete assignment was made<sup>1</sup> in line with a paper of Frankiss and Miller.<sup>5</sup> Since Rudolph *et al.*<sup>4</sup> had not observed  $\nu_6$  and  $\nu_7$ , Nešković<sup>1</sup> estimated these frequencies as 348 and 157 cm<sup>-1</sup>, respectively, on the basis of » ... *the similar spectrum of P<sub>2</sub>Cl<sub>4</sub> molecule* ... «. The frequencies of these vibrations, according to Rhee *et al.*<sup>2,\*</sup> were found to be at 514 and 103 cm<sup>-1</sup> (for solid P<sub>2</sub>F<sub>4</sub>) in a rather poor agreement with the estimated ones. Also, the value of 361 cm<sup>-1</sup> for  $\nu_{12}$ <sup>1,4</sup> is unrealistic when compared with the frequency of the related  $\nu_4$  (214 cm<sup>-1</sup>). The solid state-value (202 cm<sup>-1</sup>) should be used instead. The sequence of 12 normal modes for P<sub>2</sub>F<sub>4</sub> (combining the gas phase, liquid<sup>4</sup> and solid state-values<sup>2</sup>), which may be considered as most reliable for calculation, is given in Table I.

Using these data, the following values for the thermodynamic functions are calculated (only values up to 300 K are given):

TABLE II

*Thermodynamic functions for P<sub>2</sub>F<sub>4</sub>*

$T$ K	$C_{p,m}^0$ J · K <sup>-1</sup> · mol <sup>-1</sup>	$(H_T^0 - U_0^0)/T$ J · K <sup>-1</sup> · mol <sup>-1</sup>	$-(G_T^0 - U_0^0)/T$ J · K <sup>-1</sup> · mol <sup>-1</sup>	$S^0$ J · K <sup>-1</sup> · mol <sup>-1</sup>
100	51.8	40.1	215.2	255.3
150	64.9	46.2	232.6	278.8
200	77.0	52.4	246.7	299.1
250	87.2	58.4	259.1	317.4
300	95.6	63.9	270.2	334.1

\* In the schematic description of the modes, Rhee *et al.*<sup>2</sup> designated  $\nu_6$  and  $\nu_9$  as PF<sub>2</sub>-twist, while Frankiss and Miller<sup>5</sup> as PF<sub>2</sub>-rock, instead. The description is mainly a matter of choice, because a clear-cut distinction between twisting and rocking motions in X<sub>2</sub>Y<sub>4</sub> type molecules can be made only for planar structures or structures in which the XY<sub>2</sub> plane is perpendicular to the X-X bond.

## REFERENCES

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## SAŽETAK

**Komentar uz rad »Calculation of the Thermodynamic Function of Tetrafluorodiphosphine«**

*Vladimir Petruševski*

U nedavno objavljenoj bilješki »Calculation of the Thermodynamic Function of Tetrafluorodiphosphine« (*Croat. Chem. Acta* **63** (1990) 87) prikazan je proračun termodinamičkih funkcija za tetrafluorofosfin ( $P_2F_4$ ), u kojem se rabi aproksimacija: idealni plin/kruti rotator/harmonijsko titralo. Kritički su razmotrene postavke iz cit. bilješke koje se tiču asignacije vibracijskih spektralnih vrpca, računanja termodinamičkih funkcija i stabilnosti  $P_2F_4$ .