# High Resolution Infrared Detection of O=PF in the Gas Phase

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*Dedicated to Prof. Dr. Reinhard Schmutzler on the occasion of his 65th birthday*

Short-lived phosphenous fluoride, O=PF, has been made by flash pyrolysis of $F_2POPF_2$ in Ar at 1200°C and detected by gas phase IR spectroscopy. The $\nu_1$ band, $\nu_0 = 1297.5372$ cm$^{-1}$, has been studied with a resolution of $8 \times 10^{-3}$ cm$^{-1}$, and about 1500 transitions have been assigned. These were fitted using a Watson-type Hamiltonian, $\sigma = 1.5 \times 10^{-3}$ cm$^{-1}$, to excited state parameters up to quartic centrifugal distortion constants. The $\nu_2$ band was located at 819.58 cm$^{-1}$. An extended set of ground state parameters was obtained by combining recently measured microwave transitions with ground state combination differences formed from $\nu_1$ transitions.

The experimental results are in perfect agreement with the matrix IR spectra, mw measurements and *ab initio* calculations but disagree with a recently claimed low resolution detection of OPF in the gas phase.

*Key words:* High Resolution; Infrared Spectrum; Pyrolysis; Phosphenous Fluoride.

## 1. Introduction

Phosphenous fluoride, O=PF, belongs to the family of 18 e$^-$ species which have bent structures, and it is isovalent with well-known compounds like the very stable $SO_2$ molecule and with the less robust species $SiF_2$ and NSF. Synthetic, thermochemical, theoretical and spectroscopic aspects of the triatomic chalcogeno halides X=E-Hal, X = O, S; E = N to Sb; Hal = F, Cl, Br, have been reviewed, and the isovalence relation has been particularly addressed [1].

The OPF molecule was first obtained by the reaction of $P(O)FBr_2$ with Ag at *ca.* 980 °C and $10^{-2}$ mbar [2]. After deposition of the gas mixture with an excess of Ar the cryogenic matrix was studied by IR spectroscopy, and the three vibrational fundamentals of $^{16}$OPF were observed at 1292.2, 811.4 and 416.0 cm$^{-1}$ [2]. Measured $^{18}$O shifts and mass spectra unambiguously confirmed the first detection of OPF. Moreover, *ab initio* calculations have been performed at the SCF level and with the inclusion of electron correlation effects [2]. Recently several low-$J$ rotational transitions in the 4 - 26 GHz region have been observed of OPF, prepared by passing $PF_3/O_2$ mixtures in Ne carrier gas through an electric discharge, and $r_0$, $r_z$ and $r_e$ structures have been determined by combining experimental data with novel *ab initio* calculations [3].

A simple synthesis of OPF was recently reported by Allaf and Boustani [4]. They passed $OPCl_3$ over heated (870 °C) Ag to form OPCl and subsequently converted this to OPF by a reaction with KF at 140 °C. The products obtained, which exhibited surprisingly long lifetimes, were identified by low resolution (4 cm$^{-1}$) gas phase IR spectroscopy. Of the vibrational fundamentals of OPF, the P=O stretching vibration at 1357.2 cm$^{-1}$ is inconsistent with the matrix data (1292.2 cm$^{-1}$ [2]), and this also casts doubts on the other reported bands at 821.5 and 420 cm$^{-1}$. Moreover an absorption at 1272.8 cm$^{-1}$ was assigned to the P=O stretch of the intermediate OPCl [4]; however, this assignment does not agree well with the value recently determined on OPCl in the gas phase by high resolution TDL spectroscopy, 1263.00700(22) cm$^{-1}$ [5]. In view of the excellent agreement of the ground state rotational parameters of OP$^{35}$Cl resulting from the TDL investigation with those of a detailed microwave (mw) study [6] there is no doubt that OPCl is indeed the target molecule in these independent rovibrational and rotational studies. Moreover we note that the spectrum of the precursor $OPCl_3$ shown in Fig. 2 of [4] is indeed that of hexamethyldi-

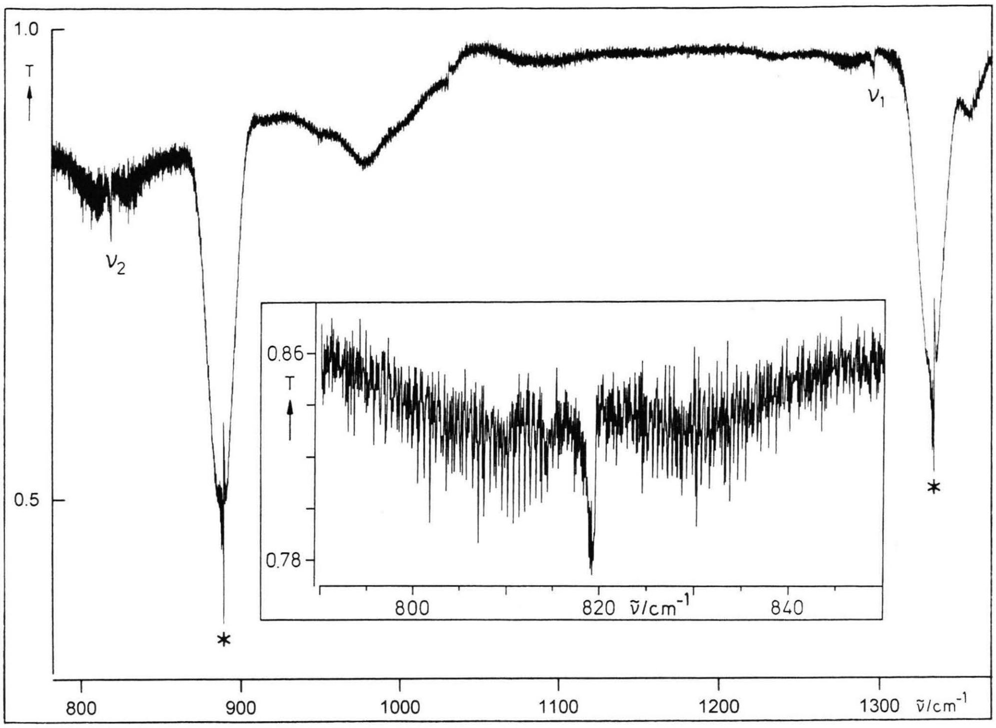

Fig. 1. Infrared spectrum (resolution 0.08 $cm^{-1}$) of the products obtained by passing $P(O)FBr_2$ in Ar over Ag wool. $\nu_1$ and $\nu_2$ denote Q branches belonging to OPF. Absorptions of $P(O)FBr_2$ are denoted by an asterisk. The insert shows the $\nu_2$ band on an expanded scale.

siloxane [7] which presumably was formed by degradation of silicon grease.

Our doubts on the claimed first observation of OPF in the gas phase by infrared spectroscopy [4] prompted us to search for this molecule by high resolution ($\geq$ 0.008 $cm^{-1}$) FTIR spectroscopy. The expected rotational fine structure would enable us to link our results to the fine and unambiguous mw work [3]. Here we report on our results.

## 2. Experimental Details

$P(O)FBr_2$ was prepared from $POBr_3$ [8] as described in [2]. $F_2POPF_2$ was synthesized according to [9]. Infrared spectra were recorded using a Bruker 120 HR interferometer equipped with a globar source, a KBr beam splitter and an MCT 800 detector. A 7 μm low-pass filter was employed.

Spectrum 1 (Fig. 1) was recorded with an effective resolution of 0.08 $cm^{-1}$, and 8 scans were collected. Spectrum 2 (Fig. 2) was obtained with an effective resolution of 0.008 $cm^{-1}$; 11 scans were coadded, and the spectrum calibrated with $H_2O$ lines in the 1350 - 1400 $cm^{-1}$ region [10].

A White-type multipass cell with a basis length of 20 cm and a total path length of 560 cm was employed. This cell, which was equipped with KBr windows, was mounted in the parallel external beam of the interferometer and connected to an external detector chamber.

A quartz inlet tube of 6 mm i. d. was inserted in the cell so that the orifice was not farther than 50 mm from the infrared beam. The innermost 30 mm of this tube were electrically heated.

First we performed an experiment analogous to that reported in [2] by evaporating $P(O)FBr_2$ kept at 25 °C in a flow of Ar and passing this gas mixture over Ag wool heated to 900 °C. In spite of the more efficient production of OPF at higher temperature [2], these conditions were chosen to prevent the melting of Ag (962 °C) and to minimize the evaporation of AgBr, though this dimmed the gold-coated mirrors of the multipass cell, and only 8 scans could be collected at medium resolution before the mirrors had to be replaced.

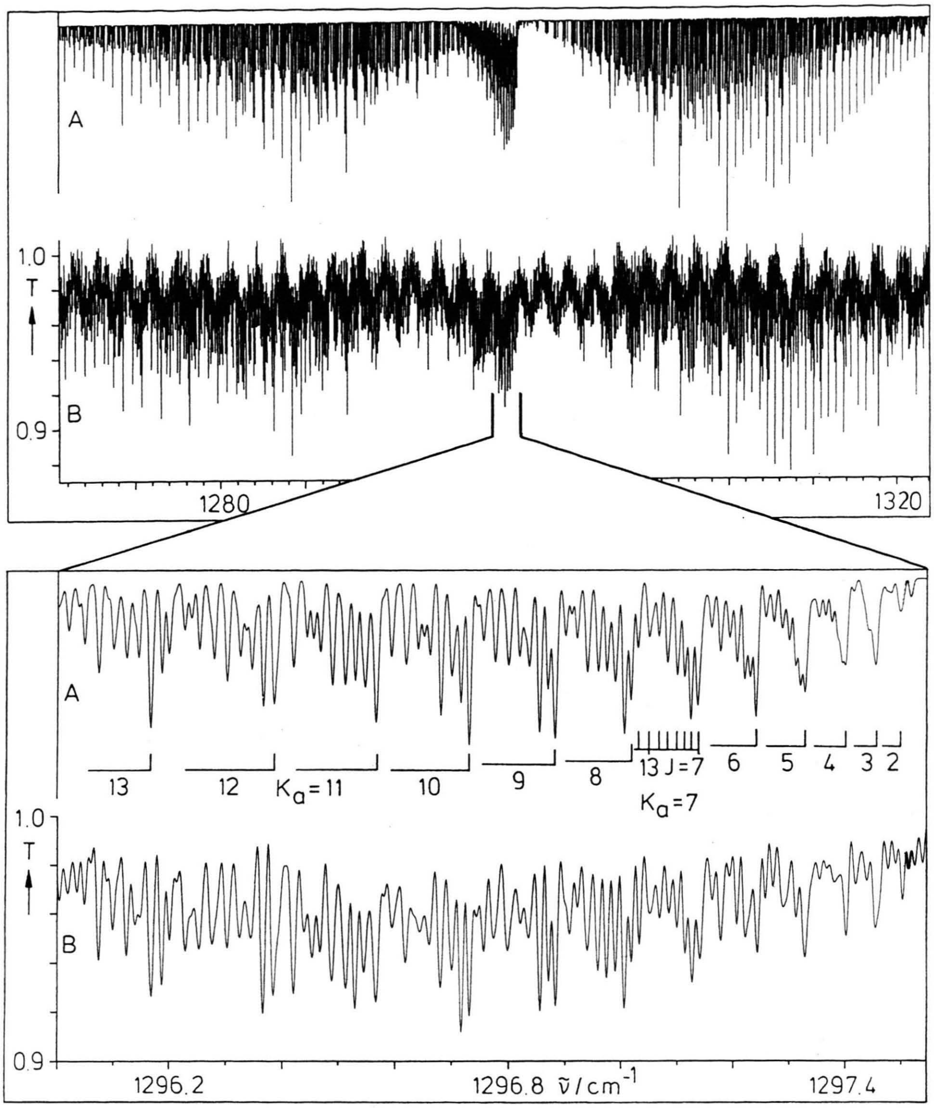

Fig. 2. The $\nu_1$ band of OPF obtained by flash pyrolysis of $F_2POPF_2$ in Ar at 1200 °C. Resolution 0.008 cm$^{-1}$. *Top:* Survey spectrum (B) and simulation (A) based on the parameters of Table 1. *Bottom:* Detail of the $\nu_1$ band in the Q branch region. A: Simulation. The $K_a$ assignment of the $^qQ_2$ to $^qQ_{13}$ branches is given, and the *J* structure of $^qQ_7$ is indicated. B: Experimental spectrum.

A pressure of 0.1 mbar was maintained in the multipass cell during the experiment. The spectrum obtained in the 750 - 1400 cm$^{-1}$ region is shown in Figure 1. There are two weak absorptions near 1298 ($\nu_1$) and 820 cm$^{-1}$ ($\nu_2$) which even at a resolution of 0.08 cm$^{-1}$ reveal some rotational fine structure. They belong to the same carrier. The spectrum is however dominated by two very strong absorptions of $P(O)FBr_2$ denoted by an asterisk at 890 and 1335 cm$^{-1}$ (880 and 1322 cm$^{-1}$, liquid phase [11]). No further absorption was detected. As in the matrix spectrum [2] and in agreement with calculations ($I(\nu_1) / I(\nu_2) = 0.4$, SCF, and 0.52, MNDO [1]) the $\nu_2$ band is about twice as strong as $\nu_1$.

Judging from the intensity of the $\nu_2$ band (PF stretch) we can roughly estimate the concentration of OPF in the flow. Assuming a homogeneous distribution in the multipass cell and the same transition moment as for $\nu_1$ of $PF_3$, we calculated a concentration of OPF of the order of $3 \times 10^{13}$ molecules per $cm^3$ in the cell.

Since the quality of the spectra, in particular the resolution that could be achieved, was not sufficient for a high resolution rovibrational analysis, we have searched for a method of generating a flow of OPF for a considerably longer time.

In analogy to the recently observed formation of $F_2Si{=}S$ with concomitant elimination of $SiF_4$ by flash thermolysis of $F_3SiSSiF_3$ [12] we have pyrolyzed 5% $F_2POPF_2$ in Ar at 1200 °C. This reaction yields OPF and $PF_3$. The flow was adjusted to 70 sccm/min, which gave a total pressure in the multipass cell of 3 mbar. A total of 11 scans were collected before the reflectivity of the mirrors in the multipass cell was significantly lowered by deposition of a solid.

The conditions of the measurement were optimized for the $\nu_1$ band at 1298 $cm^{-1}$. This band is illustrated in Figure 2. Although the $\nu_1$ and $\nu_3$ bands of $PF_3$ centered at 892 and 860 $cm^{-1}$ [13] do not interfere, the low wavenumber wing of the weak combination band $\nu_2 + \nu_4$, $\nu_0 = 834.06$ $cm^{-1}$, partly overlaps with the $^qR$ branches of $\nu_2$ of OPF.

## 3. Rovibrational Analysis

Both the $\nu_1$ and $\nu_2$ bands exhibit a parallel-type structure as expected for a predominantly a-type hybrid band of a near-prolate ($\kappa = -0.9006$) asymmetric rotor. The Q branches are structured and degraded to low wavenumber, the $^qP$ and $^qR$ branches revealing details that would be in agreement with a $(B + C)$, ca. 0.56 $cm^{-1}$ [3], modulation expected for a parallel band of OPF.

The analysis of $\nu_2$ was not persued any further because of the insufficient resolution and the poor signal / noise ratio due to the detector cut-off near 800 $cm^{-1}$. The band center of $\nu_2$, 819.58 $cm^{-1}$, was estimated from the sharp high wavenumber edge of the $^qQ$ branches. Note that the outer wing of the $^qR$ branch of the $\nu_1$ band in Fig. 1 is buried under the low-wavenumber wing ot the intense $P(O)FBr_2$ absorption; this fact further prompted us to search for an alternative synthesis of OPF.

Despite its weakness the $\nu_1$ spectrum shown in Fig. 2 is of much higher quality than that shown in Figure 1. The $^qQ$ branches offered a first assignment because the low-$K_a$ transitions are clustered and easily discernible, Figure 2. Their shape indicates that $\alpha_1^A$ is much larger than $\alpha_1^B$ and $\alpha_1^C$ and positive. As it happens, the refined $\alpha_1^A$ value of OPF, 7.98 $\times 10^{-3}$ $cm^{-1}$, is extremely close to that of OPCl, $7.94 \times 10^{-3}$ $cm^{-1}$ [5], and also of OPBr, $^{79/81}Br$ 7.85 / 7.74 $\times 10^{-3}$ $cm^{-1}$ [14]. This is understandable since the wavenumbers of the $\nu_1$ vibrations of OPF, OPCl and OPBr are very close (1298, 1263, and 1258 $cm^{-1}$), and also the $A$ constants do not differ too much (1.397, 1.120, and 1.021 $cm^{-1}$). On the other hand, $^qQ_{K_a}$ clusters of OPF are spread into individual $J$ components while those of OPCl are compressed into one single line. Of course, the similarity does not apply to $\alpha_1^B$ and $\alpha_1^C$, the $B$ and $C$ constants of OPCl being only about half those of OPF.

Some regularly spaced, strong features stand out in the $^qP$ and $^qR$ wings, Fig. 2, which were later found to belong to composites of different overlapping $K_a$ subbands. There was, however, no $K_a$ structure as obvious as in the $^qQ$ region.

The assignment of the $\nu_1$ lines was begun with the low-$J$, medium-$K_a$ ($K_a$ = 5 - 8) subband systems which do not reveal any asymmetry splittings at low $J$. The selection rules that apply to an $a$-type band are $\Delta K_a = 0$ ..., $\Delta K_c = \pm 1$ ..., and series were found starting from $^qQ$ lines with rigorous use of ground state combination differences (GSCD). These were initially based on the rotational and centrifugal distortion constants reported in [3]. As the analysis went on, more and more GSCD became available; ultimately 599 were used – their $J$ and $K_a$ values going up to 40 and 11, respectively. In spite of their limited precision of ca. $2 \times 10^{-3}$ $cm^{-1}$, these GSCD augmented the body of five mw observations with $J \leq 4$, $K_a \leq 1$ and thus enabled the refinement of additional quartic centrifugal distortion constants. With the exception of $\delta_J$, these had been constrained to their values calculated from the harmonic force field [2] in the fit of the mw observations (see below) [3].

Assignments were gradually extended to low $K_a$ series, which more and more pronouncedly exerted asymmetry splittings as $K_a$ decreased. These splittings were resolved for all lines belonging to $K_a = 1$ and 2 and for ($K_a =$, $J' \geq$): (3, 8), (4, 12), (5, 19), (6, 24), (7, 30), and (8, 37). Finally altogether 1465 IR transitions, either individual lines or doubly counted unsplit doublets, were assigned in an iterative procedure, the predictions increasing in accuracy as the analysis progressed.

## 4. Data Fit and Results

In a first step we have improved the ground state constants of OPF by combining the five mw transitions [15] assigned a weight of $10^6$ with 599 GSCD obtained from $\nu_1$ lines. These were unit-weighted when they were based on unit-weighted lines only, otherwise their weight was that of the component with the lower precision.

A Watson-type Hamiltonian reads

$$\mathcal{H}_\mathrm{w} = E_\mathrm{v} + \left(A - \frac{1}{2}(B+C)\right) J_z^2 + \frac{1}{2}(B+C)J^2 - \frac{1}{4}(B-C)J_{xy}^2 - \Delta_K J_z^4 - \Delta_{JK} J^2 J_z^2 - \Delta_J J^4 - \delta_K \{J_z^2, J_{xy}^2\} - 2\delta_J J^2 J_{xy}^2. \quad (1)$$

*A* reduction, $\mathrm{I}^r$ representation, up to quartic centrifugal distortion constants was used. All centrifugal distortion constants were refined with the exception of $\delta_K$ which was not determined with significance and therefore constrained to the value calculated from the *ab initio* force field [2]. The results of the combined fit are set out in Table 1, column 1. They are compared with the reported ground state parameters of [3], which had been obtained from the mw lines with four of the five quartic centrifugal distortion constants having been constrained to values predicted from the harmonic force field [2].

In view of the great weight assigned to the mw lines in the combined fit, the agreement to within one of their standard deviations for the refined parameters *A*, *B*, *C*, and $\delta_J$ is no surprise. However, such an agreement, albeit with larger standard deviations, is also achieved when only GSCD are fitted. It is also pleasing that the centrifugal distortion constants $\Delta_J$, $\Delta_{JK}$, and $\Delta_K$ agree with values predicted from the harmonic force field to within < 15%. The standard deviations of the combined fit, column 1, are larger by two orders of magnitude than the respective values in column 2. This is due to the larger number of refined parameters (correlation effects), the three orders of magnitude lower precision of the IR data, and the fact that the number of parameters used to fit the mw data [3] was similar to the number of observations. In view of the reproduction of the mw data with an rms of 3 kHz, which is satisfactory, we believe that the combined ground state, column 1, is presently the physically most significant one.

Table 1. Parameters of the ground (000) and $\nu_1 = 1$ (100) states of OPF. *A* reduction, $\mathrm{I}^r$ representation.

| | (000) mw + GSCD | (000) mw [3] | (100) IR |
|---|---|---|---|
| $E_\mathrm{vib}/\mathrm{cm}^{-1}$ | | | 1 297.537 24(11) |
| *A*/MHz | 41 886.49(22) | 41 886.655 9(25) | 41 647.13(12) |
| *B*/MHz | 9 288.603(22) | 9 288.599 27(44) | 9 266.936(15) |
| *C*/MHz | 7 583.319(22) | 7 583.316 26(44) | 7 562.694(11) |
| $\Delta_J$/kHz | 8.530(28) | 8.520 33[a] | 8.540 0(53) |
| $\Delta_{JK}$/kHz | –91.47(64) | –86.708 8[a] | –91.631(73) |
| $\Delta_K$/kHz | 913(145) | 1 083.77[a] | 900.8(11) |
| $\delta_J$/kHz | 2.461(15) | 2.451 3(93)[b] | 2.464 1(33) |
| $\delta_K$/kHz | 23.260 9[a] | 23.260 9[a] | 25.08(29) |
| $\Delta$/uÅ$^2$ | 0.169 56(24) | 0.169 614 3(72) | 0.154 76(14) |
| $\sigma$(Fit) mw | 3 kHz | | |
| $\sigma$(Fit) IR /$10^{-3}$cm$^{-1}$ | 1.76 | | 1.49 |

[a] Constrained to values from force constants of [2]. [b] Value from harmonic force field 2.420 54 kHz.

All this coherence of results rules out any ambiguity on the constitution of the target molecule and is moreover a proof of the reliability of the *ab initio* force field.

In the excited state parameters fit, Table 1, column 3, we have constrained the ground state parameters to those of column 1. The standard deviations of the excited state parameters, which are smaller than those of the ground state, column 1, in fact are those of the differences (*A*, *B*, *C*)"– (*A*, *B*, *C*)' etc. The rms deviation of the fit, $1.49 \times 10^{-3}$ cm$^{-1}$, has to be judged in relation to the resolution, the weakness of the band, and moreover the moderate signal / noise ratio. Many doublets that entered the refinement as two unit-weighted lines with the same wavenumber were "just not resolved" and thus spoiled the quality of the fit of altogether 1465 observations. On the other hand, many (broad) peaks composed of different $J$, $K_\mathrm{a}$ constituents were given lower weight (0.25 or 0.1).

The band contour simulation shown on traces A of Fig. 2 is in excellent agreement with the observed spectrum. This is particularly obvious for the Q branch region illustrated in the lower part of Figure 2.

Comparison of columns 1 and 3 of Table 1 reveals that the centrifugal distortion constants change only marginally upon vibrational excitation. This is a proof for the insignificance of rotational perturbations of the $\nu_1 = 1$ state. Indeed, the possible perturbers (matrix data, [2]) $\nu_2 + \nu_3$ (calc. 1227 cm$^{-1}$) and $3\nu_3$ (calc. 1248 cm$^{-1}$) are not too close to $\nu_1$.

Comparison of excited state parameters of the isosteric species SiF$_2$, OPF, NSF and SO$_2$ is of limited utility. Owing to different symmetries, the stretching vibrations $\nu_1(a_1)$ and $\nu_3(b_1)$ in $SiF_2$ and $SO_2$ cannot be compared with the P=O stretch $\nu_1$ of OPF. Moreover, Coriolis perturbations affect the $v_1 = 1$ and $v_3 = 1$ states of $SiF_2$ [16] while the (100), (020) and (001) states of $SO_2$ undergo both Coriolis and Fermi interactions [17].

Thiazyl fluoride NSF appears at first glance to be the best candidate to be compared with OPF. Again the $\nu_1$ band at 1375.6 $cm^{-1}$ is so strongly perturbed by $\nu_2 + 2\nu_3$ that it could not be completely analyzed from TDL spectra [18]. In spite of this perturbation, the $\alpha_1^A$ and $(\alpha_1^B + \alpha_1^C)$ values obtained from that analysis, 289.15 and 30.68 MHz, respectively, which are compatible with the anharmonic force field [19], have the same sign and the same magnitude as those determined for OPF, 239.4 and 42.29 MHz. We may also compare the inertial defect difference $\delta\Delta_{100} = \Delta_{100} - \Delta_{000}$, ca. –0.0094 uÅ$^2$, which is available for NSF from *ab initio* calculations at different levels [20], with that of OPF (Table 1), –0.0148 uÅ$^2$. Again both the sign and the order of magnitude are in agreement and thus further support the meaningfulness of our rovibrational analysis.

## 5. Conclusion

We have developed a new method to synthesize in the gas phase short-lived OPF by flash pyrolysis at 1200 °C of $F_2POPF_2$ in a flow of Ar. The product was characterized in the gas phase by its IR spectrum. The same spectral features were also observed when $P(O)FBr_2$ was passed over silver wool at 900 °C, as reported in the matrix IR study [2].

The spectrum of the $\nu_1$ band recorded with a resolution of ca. 0.008 $cm^{-1}$ has been rotationally analyzed. The rotational parameters determined for the ground state are in perfect agreement with those of the recent mw study [3]. Since they are complementary, their merge yields significantly improved ground state parameters including, for the first time, quartic centrifugal distortion constants. We note that these agree excellently with the corresponding values obtained by *ab initio* calculations [2]. The accurate gas phase wavenumbers of the fundamentals $\nu_1$ and $\nu_2$ are only 5 and 8 $cm^{-1}$, respectively, higher than those found in an Ar matrix [2], and they agree with their *ab initio* predictions, 1285/808 $cm^{-1}$ (MP2) [4]. Thus there remains no doubt that we have detected OPF in the gas phase by high resolution IR spectroscopy. Our observations for $\nu_1$ and, to a lesser extent, $\nu_2$ disagree with the experiments reported by Allaf and Boustani [4], and we conclude that the present study is, to the best of our knowledge, the first report of the gas phase IR spectrum of the short-lived species OPF.

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