our and others' data. However, we do not exclude the possibility that some dimeric adsorption occurs as well.

As to the conformation of the side chain, it seems to us that our conclusion reached for the side chains of adsorbed alcohols[1] is applicable here as well. We found that the term "linear" is misleading and that, in fact, the envelope of conformers is an ellipsoid with a surprisingly small ratio between the axes; for instance, in 1-butanol the deviation from a sphere is indeed small (an axes ratio of 1.2). For the acids in the present study, this is nicely illustrated in the computed silhouettes (Figures 5–9) from which it is evident that even the all-anti conformer is far from looking like a "straight narrow rod". Notice also the small variations in σ between the two conformers of butanoic acid (Tables III and IV and Figure 7). A contributing factor to the variety of the side chain adsorption conformations is the surface irregularity itself, which may force occasionally a skew-linkage on the energetically favored all-anti conformer. The "linearity" of the chain starts to show up only at relatively high lengths. Notice that the experimental value for nonanoic acid (Tables I and V and Figure 4) is somewhat smaller than the computed σ. This might reflect a partial lift-up of chains and chain overlapping as has been observed recently in an ESCA study of the adsorption of surfactants on silica.[89]

It should be stressed that our conclusions do not rest solely on the closeness of agreement between the processed experimental data and the numbers that a novel computational scheme provides. Comparison of measurement with van der Waals cross sections (Table III, numbers in parentheses) suffices, on qualitative grounds alone, to exclude the feasibility of perpendicular adsorption: the measured area changes too rapidly on going from one homologue to the next. The closeness of agreement is a result in itself, which we take to substantiate the proposed technique of estimating geometrical attributes of molecules. In practical terms, this means that it is not inappropriate to design molecular shape by using atomic coordinates and atomic radii, assigning relatively large radii to mantle-atoms. It seems indeed established nowadays that the

w solid is too small to represent a molecule, and that the larger volume obtained from liquid density (V_{mol}) provides a better approximation to size.[55,56] The pending question, apart from numerical detail, is not of volume but of shape: how should one mould the volume settled upon? Current choices are to enclose the w solid by a parallelepiped,[58] or build it up from "constant coordinate cavities" or combined fragments thereof,[90] or, alternatively, obtain the demarking surface through a quantum-chemical analysis of the charge cloud.[55] Our approach is simpler and more "chemical" than the latter choice; it may even turn out to be equivalent to it. Unlike the former options, the "reduced molecular shape" admits and preserves surface irregularities.

Coming finally back to the MH equation (eq 3), recall that our calculations also are of the "liquid-density type", but use densities only as a guide in deriving radii for mantle-atoms. Past this stage, and in dealing with specific molecules, measured densities are not referred to. It is the exploitation of shape that leads to the final estimates of cross-sectional areas. Within the bounds of error, both in measurement and in the theoretical estimate (coordinates, radii, grid method), they coincide with the experimental. Geometrical attributes of molecules have been calculated before but mainly as a tool to estimate or correlate derived quantities.[91] What we have provided here is a direct check of the attributes themselves.

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Formation and Structure of Molecular O=P–F. Mass Spectrometry, Infrared Spectra of the Matrix Isolated Species, and ab Initio Calculations[1a]

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Abstract: The molecules like SiF_2 and SO_2 are well characterized, but until now the isoelectronic compound OPF^2 has not been prepared. In the gas phase (10^{-2} mbar; 1100 K) this analogue of nitrosyl fluoride is formed by a reaction between $P(O)FBr_2$ and silver. This has been shown by mass spectrometric and matrix IR investigations (including $^{16}O/^{18}O$ shifts). By these experimental methods the following data have been obtained: $\Delta H^\circ_{298} = -404.4$ kJ/mol, IP = 12.1 eV, $\nu(PO) = 1292.2$ cm^{-1}, $\nu(PF) = 811.4$ cm^{-1}, $\delta(OPF) = 416.0$ cm^{-1}, $\angle(OPF) = 109° \pm 5°$. The results of ab initio calculations are $R_e(PO) = 145$ pm, $R_e(PF) = 157$ pm, $\angle(OPF) = 110°$, 13a' MO = 12.8 eV (Koopmans). Data obtained for OPF are compared with those of the following isoelectronic molecules: SiF_2, SO_2, NSF, ONF, NOF.

The molecules OPCl,[3] OPBr,[4] SPCl,[5] OAsCl, and OSbCl,[6,7] which are similar to nitrosyl chloride, have been described very recently. From a theoretical point of view these species are interesting as they link the long known dihalides of group IVa (14)[71]
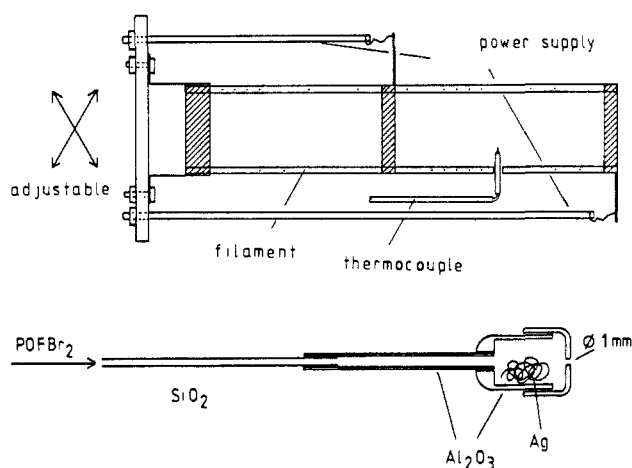
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Figure 1. Knudsen cell and Knudsen cell assembly.

elements like $SiCl_2$ with the triatomic molecules of group VIa $(16)^{71}$ atoms (O_3, S_3, SO_2). In this respect OPF is of particular interest, as it is isoelectronic to the well-known species SiF_2 and SO_2. Furthermore, there is also a similarity to the interesting molecule NSF, which is also isoelectronic to SiF_2, SO_2, and OPF. Therefore, the investigation of OPF can be very helpful in obtaining more information about the bonding situation of isoelectronic species.

OPF is not expected to be stable as a monomeric compound in a condensed state, since in such a molecule phosphorus has the unusual coordination number of 2.[8] In the gas phase $(10^{-2}$ mbar), however, OPF is found to be formed in some high-temperature reactions, e.g.

$$P(O)FBr_2 + 2Ag(s) \rightleftharpoons OPF(g) + 2AgBr(g) \qquad (I)$$

This has been proved by mass spectrometric and matrix infrared investigations. Elaborate ab initio computations have been performed—independent of and concurrent with the experimental investigations—in order to obtain data not yet accessible by experimental methods and to derive a fuller characterization of this molecule.

Technical Details

(a) Preparation of Starting Compounds. $PFCl_2$ was produced by the reaction of PCl_3 with SbF_3 (and a small amount of $SbCl_5$) followed by fractional condensation $(-76, -134, -196 °C)$ to remove PCl_3, PF_2Cl, and PF_3. The purity of $PFCl_2$ is 99%; it must be stored at $-196 °C$ to prevent formation of PF_3, PCl_3, and PF_2Cl as well as an attack of the glass walls generating SiF_4.

$P(O)FCl_2$ was obtained by the fluorination of $P(O)Cl_3$ with thoroughly dried NH_4F at 0 °C. By fractional condensation $P(O)Cl_3$, $P(O)F_2Cl$, and $P(O)F_3$ can be removed, giving a purity of 99.5%. Storage of this compound is not as critical as that of $PFCl_2$.

$P(O)FBr_2$ was prepared by the reaction of $P(O)Br_3$ with SbF_3 as the fluorinating agent. The reaction products $P(O)F_3$, $P(O)F_2Br$, and $P(O)FBr_2$ were separated and purified by fractional condensation. During this procedure the purity of $P(O)FBr_2$ was

monitored by repeted mass spectrometric measurements. IR and Raman spectra of all compounds discussed here agree with those reported earlier.[9]

(b) Mass Spectrometry. In order to ensure identical composition the high-temperature vapor being condensed into the matrix and of the vapor analyzed by the mass spectrometer, the same furnace assembly was used in both methods. A schematic view of our arrangement and the Knudsen cell is given in Figure 1. The furnace assembly can be adjusted such that the molecular beam leaving the evaporation orifice of the Knudsen cell gives a maximum intensity of the ions in the mass spectrum. The corundum oven is heated by a tungsten filament and covered by a tantalum shield. The temperature is measured by a Pt/Pt–Rh thermocouple. The silver-containing Knudsen cell is connected with the $P(O)FBr_2$ reservoir by means of a flexible tube (PTFE).

For mass spectral analysis we used an Extranuclear Quadrupol mass spectrometer (ionization by electron impact, 70 eV). Appearance potential curves were registrated by an x–y recorder with ethylene as the calibration gas.

(c) Matrix Isolation and IR Spectroscopy. In addition to the starting compounds described above, the isotopomer $P(^{18}O)FCl_2$ had to be prepared so as to generate ^{18}OPF. This, in turn, was used to check the vibrational assignments and to confine the range of the force field parameters. $P(^{18}O)FCl_2$ can be obtained either in a direct reaction between $PFCl_2$ with $^{18}O_2$[10] or by passing a mixture of $^{18}O_2$ and $P(^{16}O)FCl_2$ over heated silver at 1500 K in an Al_2O_3 tube.[11] The latter is experimentally more convenient.

Mass spectroscopic experiments starting with $P(O)FCl_2$ have shown that, at 1500 K, there is almost no starting material present in the equilibrium mixture. But under such conditions Ag evaporates to a large extent, causing the matrix to darken. At lower temperatures, however, only small amounts of OPF can be obtained. Therefore $P(O)FBr_2$ was used as a starting compound as described in the mass spectrometric section. The lower formation temperature makes this a good method both for matrix experiments and for mass spectrometric investigations.[13] ^{18}O PF was obtained by passing a mixture of $P(O)FBr_2/^{18}O_2$ over heated Ag.

All spectra discussed in this paper have been obtained by a reaction of $P(O)FBr_2$.[14]

Stainless steel valves are heavily attacked by $P(O)X_3$ compounds. Therefore, to obtain good matrix spectra it was better to regulate the amount of starting material by means of controlling the vapor pressure of the sample by cooling [$P(O)FBr_2$ was cooled to -40 to $-15 °C$].

The matrix experiments were performed with a variable continous flow cryostat employing liquid helium. This cryostat can be rotated through 90° relative to the outer fixed vacuum shroud so that the cold surface can face the orifice of the Knudsen cell in one position or the light source of the IR spectrometer (PE 225) in the other.[15] The spectra were measured in transmission with a reflection unit (cold Cu surface). Generally the high-temperature gas mixture was deposited together with an excess of Ar.

(1) (a) Presented in part at the international Matrix Conference, 1985, Fontevraud. (b) University of Karlsruhe. (c) University of Münster.

(2) To avoid confusion, all ABC molecules discussed in this text are written in the sequence of the atoms involved.

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(9) Müller, A.; Niecke, E.; Glemser, O. *Z. Anorg. Allg. Chem.* **1967**, *350*, 246.

(10) At 550 K $PFCl_2$ reacts in a sealed glass ampule with $^{18}O_2$ to $P^{18}OFCl_2$.

(11) Under these conditions the ratio $^{16}OPF/^{18}OPF$ can increase up to 1. Without silver there is no $^{16}O/^{18}O$ exchange observed, indicating that such a reaction can only proceed in the presence of an "intermediate" like OPF with a low coordinated P atom. In an equilibrium with O_2 via PO_2F^{12} a $^{16}O/^{18}O$ exchange is possible.

(12) Ahlrichs, R.; Ehrhardt, C.; Lakenbrink, M.; Schunck, S.; Schnöckel, H. *J. Am. Chem. Soc.*, accepted for publication.

(13) OPF concentrations in the matrix are now sufficiently high to observe the two intense stretching vibrations as well as the bending mode with its low intensity.

(14) Reactions starting with $P(O)FCl_2$ at higher temperatures favor more side reactions, e.g., with the furnace, and therefore such spectra are much more complicated. But nevertheless they confirm the results presented here. The small $^{16}O/^{18}O$ shift of $\nu(PF)$ could only be measured in experiments with a sufficiently hgih ^{18}OPF concentration [only possible starting with $P(^{18}O)FCl_2$].

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Table I. Mass Spectrometrically Observed I(obsd) in the System $P(O)FBr_2/Ag$ and Distribution of the Observed Intensities to the Neutral Molecules OPF and $P(O)FBr_2$: $I(P(O)FBr_2)$ and I(OPF)

ion/int.	1021 K intensities[a]			1084 K intensities			1148 K intensities		
	obsd	$P(O)FBr_2$	OPF	obsd	$P(O)FBr_2$	OPF	obsd	$P(O)FBr_2$	OPF
P^+	54	15	39	50	6	44	50	1	49
PO^+	630	96	534	640	35	615	670	4	666
PF^+	173	37	136	170	14	156	170	2	168
POF^+	1195	65	1130	1310	24	1286	1370	3	1367
Ag^+	225	0	0	254	0	0	606	0	0
PBr^+	6	6	0	0	0	0	0	0	0
$POFBr^+$	438	438	0	159	159	0	18	18	0
$AgBr^+$	850	0	0	891	0	0	1032	0	0
$POFBr_2^+$	31	31	0	12	12	0	2	2	0

[a] Absolute intensities in arbitrary units.

$^{18}O_2$ samples were purchased from Prochem (London).

(d) Details of Computation. The calculations were done on the SCF level and with the inclusion of effects of electron correlation by means of single-reference CI(SD) and CPF (coupled pair functional) computations.[16] The recently proposed CPF method may be considered as a size-consistent modification of the CI(SD) technique. This is achieved by including effects of higher than doubly substituted functions—so called cluster corrections—in an approximate way related to CEPA-1.[17] All valence MOs were correlated in CI(SD) and CPF treatments.

All computations were performed with the Karlsruhe version[18] of the Columbus system of programms.[19,20] The following basis set was used

$$P: \ (11,7,2,1)/[7,4,2,1], \ \eta_d = 0.96; \ 0.32$$

$$\eta_f = 0.6$$

$$O,F: \ (9,5,1,1)/[5,3,1,1], \ \eta_d(O) = 1.25; \ \eta_d(F) = 1.4$$

$$\eta_f(O) = 1.5; \ \eta_f(F) = 1.68$$

This basis is sufficiently flexible to yield SCF results close to the HF limit but is still not large enough to predict, e.g., equilibrium distances with an accuracy better than 1 pm.

The electronic structure of OPF (alongside some closely related molecules) has also been investigated with the aid of a population analysis of the SCF wave function. For this purpose we applied the population analysis based on occupation numbers[21-24] of modified atomic orbitals (MAO).[23] Details of the actual method are described elsewhere,[24] but it appears appropriate to give a shorthand description. The electronic structure is characterized by atomic net charges, Q_A for atom A, and by shared electron numbers, SEN(A,B), describing (almost literally) the number of electrons shared by the atoms A and B. This procedure has two basic advantages over the Mulliken population analysis:[25] (i) the results, i.e., the Q_A and the SEN(A,B), are relatively stable quantities and depend little on the actual basis set used; and (ii) the SEN(A,B) have been shown to be a reliable measure of covalent bond strength, i.e., they correlate strongly with the bond dissociation energy of covalent bonds.[24,26]

Results

(a) Mass Spectrometry. (i) Qualitative Identification of OPF. The formation of OPF by the high-temperature reaction between

Figure 2. Appearance potential curve of POF^+.

$P(O)FBr_2(g)$ and solid silver (1) is indicated by three observations: (1) the rapid change of relative intensities for the phosphorus-containing ions in the mass spectrum; (2) the formation of silver bromide; and (3) the low appearance potential of POF^+. Observations 1 and 2 are demonstrated by comparison of the mass spectra at 298 and 1148 K [relative intensities at 298/1148 K in brackets ($I(POF^+) = 1000$)]: $P^+(234/36)$, PO^+ (1471/489), PF^+ (571/124), POF^+ (1000/1000), Ag^+ (0/442), PBr^+ (129,0), $POFBr^+$ (6714/13), $AgBr^+$ (0/753), $POFBr_2^+$ (1657/1).

The intensities of the strongest ions at 298 K ($POFBr^+$ and $POFBr_2^+$) formed by fragmentation of $P(O)FBr_2$ decrease at 1148 K to values near zero, which indicates that there are only small amounts of $P(O)FBr_2$ in the high-temperature equilibrium.

The measured appearance potential curve (AP = 12.1 eV)[27] is given in Figure 2.

(ii) Thermodynamic Stability of OPF. By using the van't Hoff equation, the enthalpy of reaction can be calculated by second law or third law methods. We used the third law method, because the entropy of reaction I and change of molecular heats are well-known from the analogous reaction

$$P(O)Cl_3(g) + 2Ag(s) = OPCl(g) + 2AgCl(g) \quad \text{(II)}$$

$$\Delta_R S°_{298} = 353.4 \ J/(K \cdot mol); \ \Delta c_{p,298} = -17.5 \ J/(K \cdot mol)^3$$

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(26) In order to give the reader an idea of the numbers involved we report some typical examples: normal single bonds, SEN $\approx$ 1.4 (C—C, C—H); normal double bonds, SEN $\approx$ 2.2 (C=C); normal triple bonds, SEN $\approx$ 3.0 (C≡C, N≡N); weak single bonds, SEN $\approx$ 1.0 (Cl—Cl) to 0.7 (F—F); polar single bonds, SEN $\approx$ 1.0 (H—F) to 0.3 (NaF).

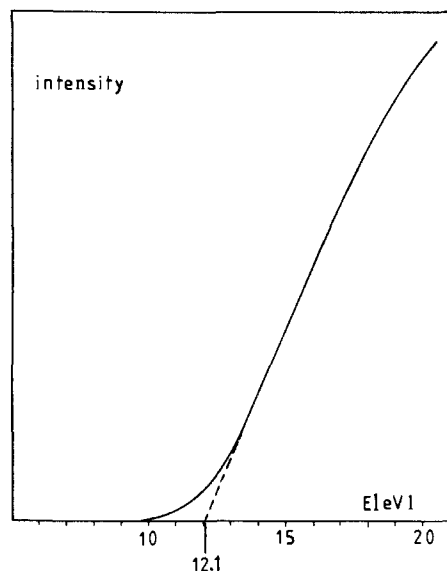(27) Literature data about AP measurements of POF^+ formed by fragmentation processes (e.g., from $P(O)F_3$) are not available. But a comparison with data given for fragmentation of $P(O)Cl_3$ seems helpful: An AP of the fragment ion $POCl^+$ of 15.6 eV[28] has been obtained. Our measured value of AP(POF^+) = 12.1 eV is much lower, indicating this ion to be formed by direct ionization of the OPF molecule and not by the fragmentation process. Within the limit of error (about ±0.5 eV) the measured value agrees with that calculated by ab initio methods (v.i.).

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The partial pressure of a mass spectrometrically observed species i is given by the equation

$$p_i = c\sum I T / \sigma_i \qquad (1)$$

where p_i = partial pressure of i; c = calibration factor;[29] $\sum I$ = sum of intensities of all ions formed by the fragmentation process of species i; and σ_i = ionization cross section of i.[32]

To calculate equilibrium constants of a reaction by means of mass spectrometry, it is necessary to observe the starting compounds as well as the reaction products in the same experiment. This leads to a superposition of the ion intensities of P^+, PO^+, PF^+, and POF^+. These ions have two precursors, OPF and $P(O)FBr_2$. From the knowledge of the mass spectrum of pure $P(O)FBr_2$ it is possible to distribute the measured superimposed intensities of these ions to the individual molecules OPF and $P(O)FBr_2$. The peak of $POFBr^+$ was chosen as reference. This ion is only formed by fragmentation of $P(O)FBr_2$, of which the following mass spectrum (298 K, 70 eV) has been measured (intensities in parentheses): P^+ (82), PO^+ (515), PF^+ (200), POF^+ (350), PBr^+ (45), $POFBr^+$ (2350), $POFBr_2^+$ (580).

The measured intensities and partial intensities formed by fragmentation of OPF and $P(O)FBr_2$ at 1021, 1084, and 1148 K are listed in Table I. With the help of these values $\sum I$ values can now be calculated (see eq 1).

$$T = 1021 \text{ K:}\quad \sum I(\text{OPF}) = 1839,\ \sum I(\text{P(O)FBr}_2) = 688,$$
$$\sum I(\text{AgBr}) = 1075$$

$$T = 1084 \text{ K:}\quad \sum I(\text{OPF}) = 2101,\ \sum I(\text{P(O)FBr}_2) = 238,$$
$$\sum I(\text{AgBr}) = 1145$$

$$T = 1148 \text{ K:}\quad \sum I(\text{OPF}) = 2250,\ \sum I(\text{P(O)FBr}_2) = 30,$$
$$\sum I(\text{AgBr}) = 1638$$

In connection with the calibration factor c^{29} and the cross sections,[32] the following values of partial pressures [bar] result:

$$T = 1021 \text{ K:}\quad p(\text{OPF}) = 7.94 \times 10^{-6},\ p(\text{P(O)FBr}_2) =$$
$$1.44 \times 10^{-6},\ p(\text{AgBr}) = 2.78 \times 10^{-6}$$

$$T = 1084 \text{ K:}\quad p(\text{OPF}) = 9.63 \times 10^{-6},\ p(\text{P(O)FBr}_2) =$$
$$5.30 \times 10^{-7},\ p(\text{AgBr}) = 3.14 \times 10^{-6}$$

$$T = 1148 \text{ K:}\quad p(\text{OPF}) = 1.09 \times 10^{-5},\ p(\text{P(O)FBr}_2) =$$
$$7.07 \times 10^{-8},\ p(\text{AgBr}) = 4.75 \times 10^{-6}$$

According to reaction I one would expect the partial pressure of AgBr to be two times higher than the pressure of OPF. The measured values of $p(\text{AgBr})$ are, however, somewhat smaller. This may be caused by the fact that some silver bromide leaves the Knudsen cell not through the evaporation orifice but through the supply line for $P(O)FBr_2$ and condenses in its colder parts. For
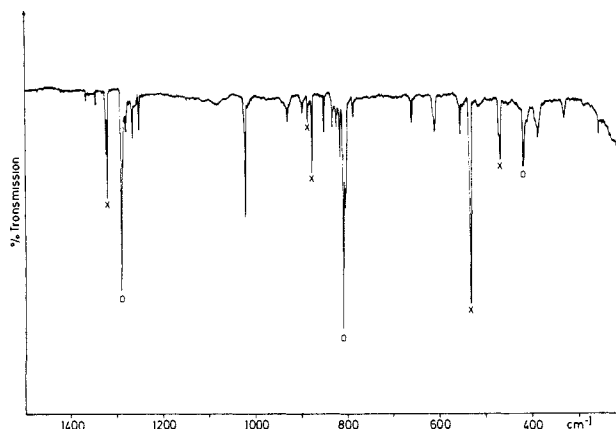

Figure 3. Infrared spectrum of a high-temperature (1250 K) gas mixture (eq 1) deposited in an Ar matrix. The absorptions of the most prominent species are marked as follows: $P(O)FBr_2$ (×) OPF (O).

this reason it is difficult to calculate correct values of Kp on the basis of the measured partial pressures. One possible way (method A) of evaluation of the measurements is to substitute $p(\text{AgBr})$ by $2p(\text{OPF})$. This leads to

$$Kp = 4p^3(\text{OPF})/p(\text{P(O)FBr}_2)$$

The other method of analyzing the data (method B) is to calculate the equilibrium constants on the basis of the measured AgBr pressures. Together with the entropy of reaction I and change of molar heats the following values of Kp and $\Delta_R H^\circ_{298}$ can be calculated.

	Kp[bar^2]	$\Delta_R H^\circ_{298}$ [kJ/mol]
evaluation (A):		
1021 K:	1.39×10^{-9}	524.7
1084 K:	6.74×10^{-9}	542.2
1148 K:	7.32×10^{-8}	550.6
		mean value 539.2
evaluation (B):		
1021 K:	4.26×10^{-11}	554.2
1084 K:	1.79×10^{-10}	574.6
1148 K:	3.48×10^{-9}	579.4
		mean value 569.4

Our experimental results do not allow use to decide which of the two values is the correct one. The temperature drift of ΔH° values as well as the differences between ΔH° (method A) and ΔH° (method B) indicate an unusually low accuracy of the calculated heat of formation. An accuracy of ± 30 kJ/mol is estimated.

On the basis of $\Delta_R H^\circ_{298}$ = 539.2 kJ/mol and in connection with the heats of formation [kJ/mol] of the compounds $P(O)FBr_2(g)$ (−681.6),[36] AgBr(g) (131.0),[30] $P_1(g)$ (333.9),[37] $O_1(g)$ (249.4),[37] and $F_1(g)$ (76.8),[37] the following heats of formation and atomization can be calculated: $\Delta H^\circ_{298}(\text{OPF}(g))$ = −404.4 kJ/mol, $\Delta H_{a1\ 298}(\text{OPF}(g))$ = 1064.5 kJ/mol.

(b) IR Spectra of the Matrix-Isolated Species. When the equilibrium gas mixture produced by the reaction of $P(O)FBr_2$ with Ag at 1250 K is deposited with an excess of Ar on a helium-cooled surface, the IR spectrum shown in Figure 3 is observed. As the concentration of guest molecules in this matrix is somewhat high (1:200), some bands exhibit complicated features caused by aggregation.[38] Absorptions of the starting compound $P(O)FBr_2$ are marked.[39] The other most prominent absorptions are those

(29) The calibration factor was determined by measuring the saturation pressure of solid silver at 1261 K. An intensity $I(\text{Ag}^+)$ of 1795 (arbitrary units) has been observed. The vapor pressure of silver at 1261 K is 5.88 × 10⁻⁶ bar.[30] In connection with the ionization cross section of silver (σ_{Ag} = 11.4 × 10⁴ pm²)[31] a value of c = 2.96 × 10⁻⁷ bar pm²/K results.

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(32) One possibility to calculate the cross section of a molecule is to add the cross sections of the elements of the compound.[33] It has been shown earlier that values calculated this way are somewhat too high (e.g., ref 34). To get an appropriate approximation,[35] cross sections obtained by this method have been multiplied by a factor of 0.7. We used the cross sections of the elements given by Stafford.[31] P, 4.4 × 10⁴ pm²; O, 3.2 × 10⁴ pm²; F, 2.4 × 10⁴ pm²; Br, 5.3 × 10⁴ pm²; Ag, 11.4 × 10⁴ pm²) and obtained for $\sigma(\text{OPF})$ = 7.0 × 10⁴ pm², $\sigma(\text{P(O)FBr}_2)$ = 14.4 × 10⁴ pm², and $\sigma(\text{AgBr})$ = 11.7 × 10⁴ pm².

(33) Otvos, J. W.; Stevenson, D. P. *J. Am. Chem. Soc.* 1956, 78, 546.

(34) Berkowitz, J.; Tashman, H. A.; Chuspka, W. A. *J. Chem. Phys.* 1962, 36, 2170.

(35) Neubert, A. *High Temp. Sci.* 1978, 10, 261.

(36) Binnewies, M.; Borrmann, H. *Thermochim. Acta*, in press.

(37) Stull, D. R.; Prophet, H. *Janaf Thermochemical Tables*; US Department of Commerce, National Bureau of Standards: Washington, 1971.

(38) Experiments with higher dilution exhibit only single bands; but under these conditions the weak absorption of the δ-mode cannot be observed.

(39) The following frequencies of $P(O)FBr_2$ have been observed[9] (cm⁻¹): 1325 (s), 1322 (vs), 890 (s), 880 (vs), 536 (sh), 532 (vs), 456 (s).

Table II. Calculated Force Constants[a,d] and Isotopic Shifts[b] of OPF[c]

							$\Delta\nu$	
$F[\nu(PO)]$	$F[\nu(PO)/\nu(PF)]$	$F[\nu(PO)/\delta(OPF)]$	$F[\nu(PF)]$	$F[\nu(PF)/\delta(OPF)]$	$F[\delta(OPF)]$	$\nu(PO)$	$\nu(PF)$	$\delta(OPF)$
10.33	0.05	0.2	4.75	0.2	0.62	46.98	1.34	10.02
10.35	0.1	0.2	4.74	0.2	0.62	47.14	1.29	10.02
10.30	0.1	0.1	4.73	0.2	0.62	46.90	1.20	10.15
10.37	0.1	0.2	4.64	0.1	0.62	47.35	1.12	10.04

[a] mdyn Å^{-1}; normalized to PO distance. [b] $^{16}O/^{18}O$; cm^{-1}. [c] This calculation based on the following: $\nu(PO) = 1292.2$ cm^{-1}; $\nu(PF) = 811.4$ cm^{-1}; $\delta(OPF) = 416.0$ cm^{-1}. The following isotopic shifts ($^{16}O/^{18}O$ cm^{-1}) have been observed (corrected values in brackets):[47] $\Delta\nu(PO) = 47.0$ (47.4); $\Delta\nu(PF) = 9.8$ (9.9); $\Delta\delta(OPF) = 1.0$ (1.0); accuracy for all measured values is ±0.2 cm^{-1}. [d] For this molecule symmetry adapted force constants (F) are identical with internal force constants (f).

Table III. Computed Properties of OPF, SO$_2$, and NSF in Comparison with Available Experimental Data[a]

molecule	method[b]	$R_e(XY)$	$R_e(YZ)$	XYZ	μ	E^f
OPF	SCF	142.6	154.9	109.9	2.5	−515.124 19
	CI(SD)	144.0	155.9	109.7	2.2	−515.649 89
	CPF	145.6	157.6	110.0	1.8	−515.718 08
	exptl					
SO$_2$	SCF	139.6		118.1	2.2	−547.237 26
	CI(SD)	141.7		118.7	1.9	−547.782 03
	CPF	143.8		118.9	1.5	−547.862 58
	exp[c]	143.2		119.5	1.6	
NSF[d]	SCF[g]	(143.6)	(162.6)	(113.1)	(2.2)	−551.318 47
	CI(SD)	142.7	161.0	(117.0)	2.0	−551.878 51
	CPF	145.9	164.7	(117.0)	1.9	−551.927 71
	exptl.[e]	144.8	164.3	117.0	1.9	

[a] Distances in pm, dipol moment μ in D, total energy in au. [b] Method of computation and basis set used as described in the text. [c] Reference 69. [d] Reference 70. Angle fixed. [e] Reference 49. [f] At the given geometry. [g] 1d on S, N, F.

at 1292 and 812 cm^{-1}. They are in the region expected for the stretching vibrations of an OPF molecule which should be one of the most abundant species in such an equilibrium (vs. mass spectroscopy). Apart from these bands some additional ones of moderate intensity have to be assigned to SiF$_4$ (1023, 384 cm^{-1}), CO$_2$ (662 cm^{-1}), P(O)F$_2$Br (1366, 935, 554 cm^{-1}),[9] and OPBr (1252 cm^{-1}).[4,40]

In former experiments starting with P(O)FCl$_2$[41] the two stretching vibrations of OPF at 1292 and 811 cm^{-1} have also been observed; but in this case the frequency of the bending mode with its much lower intensity had not been recorded. However, an additional absorption at 416 cm^{-1} (the expected region for a OPF deformation mode[42]) was observed in the P(O)FBr$_2$ experiment described above, where the OPF concentration was higher. Support for this assignment, and for those of the stretching vibrations, comes from experiments with ^{18}O-enriched samples (v.s. normal coordinate analysis.

Normal Coordinate Analysis. The harmonics of OPF isolated in an Ar matrix and their experimentally determined $^{16}O^{18}O$ shifts are listed in Table II. After correlation for anharmonicity (in parentheses),[47] they can be compared with those calculated by normal coordinate analysis. In this triatomic molecule (C_s symmetry) all vibrations belong to the same representation (A′). On the basis of the three harmonics and their isotopic shifts a bond angle of 109 ± 5° can be calculated assuming reasonable interaction force constants.[48] But as the possible range for the geometry of OPF can be confined more accurately by ab initio methods (v.i.), the results of normal coordinate calculations

presented here are based on the structure obtained by such quantum-mechanical computations:

$$r(PO) = 145 \text{ pm}, \ r(PF) = 157 \text{ pm}, \ \angle OPF = 110°$$

Furthermore, Table II shows some calculated $^{16}O/^{18}O$ shifts obtained with different sets of force constants. The best fit is achieved by the following set:

$F[\nu(PO)]$	$F[\nu(PO)/\nu(PF)]$	$F[\nu(PO)/\delta(OPF)]$
10.3 ± 0.05	0.1 ± 0.1	0.2 ± 0.1

$F[\nu(PF)]$	$F[\nu(PF)/\delta(OPF)]$	$F[\delta(OPF)]$
4.70 ± 0.05	0.1 ± 0.1	0.62 ± 0.01

All constants are given in mdyn Å^{-1} and those including the bending coordinate are normalized to the PO distance.

(c) Ab Initio Calculations. (i) Geometry and Dipole Moment. In Table III we have collected computed properties of OPF and the related isoelectronic molecules SO$_2$ and NSF as obtained by SCF, CI(SD), and CPF methods. Identical sets of basis sets were employed for all molecules. Since experimental data are available for NSF and SO$_2$, this allows us to assess the accuracy of the respective methods of computation.

Equilibrium distances are usually underestimated within the SCF approximation, by up to ≈4 pm for the cases considered, at least for sufficiently large basis sets. This is rectified to some extent on the CI(SD) level, which still yields small R_e (by up to ≈2 pm as compared to experiment), however. These deficiencies can be safety attributed to the violation of the size consistency requirement by the CI(SD) procedure.[16] The CPF results for R_e are up to ≈1 pm larger than experiment for the basis set used and are clearly the most accurate among the methods applied. A further extension of the basis set is expected to have little effect on the SCF geometry but will further shorten computed bond distances for the CI(SD) and the CPF method. This further increases the discrepancy between CI(SD) and experiment but reduces the deviation between CPF and experiment.

On the basis of a comparison of computed CPF (within the present basis set) and experimental geometries (which may also be in error by up to ≈1 pm[49]) and by means of the authors' general

(40) Weaker absorptions which are not assigned are observed at 1346, 1288, 1282, 902, 853, 826, 789, 612 (br), 425, 324, 285, and 25o cm^{-1}.

(41) These experiments are not discussed here.[14]

(42) This has been concluded by comparing a list of the following molecules (cm^{-1}): OPCl, 308;[3] ONCl, 332;[43] ONF, 520;[44] NSF, 366;[45] SSO, 382.[46]

(43) Jones, L. H. *Inorganic Vibrational Spectroscopy*; Marcel Dekker: New York, 1971.

(44) Jones, L. H.; Asprey, L. B.; Ryan, R. R. *J. Chem. Phys.* **1967**, *47*, 3371. Ryan, R. R.; Jones, L. H. *J. Chem. Phys.* **1969**, *50*, 1492.

(45) Mirri, A. M.; Guarnieri, A. *Spectrochim. Acta, Part A* **1967**, *23*, 2159.

(46) Tang, S.-Y.; Brown, C. W. *Inorg. Chem.* **1975**, *14*, 2856.

(47) Becher, H. J. *Fortschritte Der Chemischen Forschung*; Springer: Berlin, 1968; Bd. 10.

(48) See below discussion of force constants.

(49) Kirchhoff, W. H.; Wilson, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1726. Cook, R. L.; Kirchhoff, W. H. *J. Chem. Phys.* **1967**, *47*, 4521.

experience we estimate the following structure parameters of OPF: $R_e(OP) = 144.8 \pm 0.6$ pm; $R_e(PF) = 157.3 \pm 0.3$ pm; $\angle(OPF) = 110 \pm 1°$. The computed dipole moments also display the expected pattern: μ is considerably overestimated on the SCF level, and the CI(SD) value is much closer to experiment from which the CPF result deviates by 0.1 D. We therefore estimate the accurate dipole moment as $\mu = 1.8 \pm 0.15$ D.

(ii) Ionization Potential. The smallest vertical ionization potential—corresponding to the removal of a 13a′ electron—computed by means of various methods: Koopmans' theorem, 12.8 eV; ΔE_{SCF}, 11.2 eV; ΔE_{CI}, 12.0 eV; ΔE_{CPF}, 12.0 eV.

The corresponding ΔE values are obtained from the energies of independent computations of the corresponding $^1A'$ state of POF and the $^2A'$ state of the cation. CPF and CI(SD) results are virtually identical since to a large extent cluster corrections cancel out, because they are of comparable magnitude for the molecule and its cation. The CI(SD) and the CPF results should be in error by a few tenths of an eV, at most. The values obtained are in good agreement with the ionization potential determined experimentally (12.1 eV; v.s.).

(iii) Population Analysis. These results are presented in subsection c under Discussion, because they are more informative in connection with data of other molecules.

Discussion

(a) Thermochemistry. With the help of thermodynamic data obtained for OPF it is now possible to compare the thermodynamic stability of this molecule with those of the isoelectronic species SiF_2 and SO_2. The following values for the heat of atomization (298 K, kJ/mol), SiF_2 1114.6,[37] OPF 1064.5, and SO_2 1032.8,[30] show an increase of stability with growing polarity of the bonds. The same is valid for another isoelectronic series including the SPCl molecule which has been discussed by us some time ago: $SiCl_2$ 857.1,[37] SPCl, 745.9,[5] and S_3, 690.5.[37] As in the former series stability increases in direction to the silicon dihalide. From a thermochemical point of view molecules like OPF and SPCl show a "normal" behavior. Our results further demonstrate the possibility to interpolate the thermodynamic stability of isoelectronic species.

Since the heat of atomization is identical with the sum of bond energies, e.g., the bond energy of the Si–F bond in SiF_2 is 557.3 kJ/mol, such values should be a good measurement for the bond strength. But the "usual" idea of bond strength is obviously different, since double bonds in SO_2 should be stronger than single bonds in SiF_2, which is just opposite to the bond energies discussed above. This comparison shows clearly that it is not possible to describe a bond by a single numerical value. "Chemical feeling" of bond strength is better described by force constants and SEN (or sometimes distances) than by bond energies. Therefore the former ones are discussed in the following sections.

(b) Force Constants. All interaction force constants obtained for OPF are paralleled by those of comparable molecules: The bond–bond interaction force constant $P(PO/PF)$ has a value of 0.1 mdyn Å^{-1}. This is in line with the corresponding constants in the isoelectronic molecules SO_2 (0.08),[50] SiF_2 (0.31),[51] and NSF (0.01).[45] Furthermore, the value of this interaction constant fits in with that obtained after an extrapolation of the corresponding values of the following molecules: $OPCl^3$ (0.04 mdyn Å^{-1}), ONCl and ONF[43,44] (1.5o and 2.24 mdyn Å^{-1}). The bond–angle interaction force constants of OPF are 0.2 ± 0.1 mdyn Å^{-1} for $F(PO/\angle OPF)$ and 0.1 ± 0.1 mdyn Å^{-1} for $F(PF/\angle OPF)$. Both constants are normalized to $r(PO)$.[52] These values are in line with $F(r/\delta)$ of some other triatomic molecules with 18 valence electrons as well:[53]

$f(NO/\delta)$		$f(NF/\delta)$	$f(NCl/\delta)$	$f(PO/\delta)$	$f(PCl/\delta)$
0.26	0.09	0.145	0.06	0.04	0.1
ONF	ONCl	ONF	ONCl	OPCl	OPCl

$f(SO/\delta)$	$f(SiF/\delta)$	$f(SN/\delta)$	$f(SF/\delta)$
0.23	0.13	(−)0.04	0.02
SO_2	SiF_2	NSF	NSF

The values of the diagonal force constants in OPF are also as expected. $f(PO)$ has been calculated to be 10.3 mdyn Å^{-1} which is, as expected, a little larger than in OPCl (9.8 mdyn Å^{-1}) and smaller than this constant in $P(O)F_3$ (11.0 mdyn Å^{-1}).[54,55] $f(PF)$, with a value of 4.7 mdyn Å^{-1} for OPF, is interesting too. It increases going to PF_3 (5.4 mdyn Å^{-1})[56] and to $P(O)F_3$ (6.3 mdyn Å^{-1}),[54] which parallels the change of the coordination number from 2 to 4. This is consistent with the trend found for the corresponding distances which decrease from 157 to 152 pm.[56,58]

Summarized force constants and distances in OPF are best compared with those of SO_2 and SiF_2: 10.3 mdyn Å^{-1}, 143 pm (SO_2);[50] 5.5 mdyn Å^{-1}, 159 pm (SiF_2).[51] Thus, as regards its bonding, OPF is central between SiF_2 and SO_2. The same is true for the bond angle and the deformation force constant. These structural parameters increase in the sequence $SiF_2 \rightarrow POF \rightarrow SO_2$:

101°	110°	119°	
0.44	0.57	0.82	mdyn Å^{-1} [59]

Furthermore, the calculated force constants of OPF are plausible when compared with those of another isoelectronic molecule: NSF, for which the following force constants have been obtained (mdyn Å^{-1}):[45,60]

$$F[\nu(SN)] = 10.7; \quad F[\nu(SF)] = 2.9; \quad F[\delta(NSF)] = 0.44;$$

$$F[\nu(SN)/\nu(SF)] = 0.1; \quad F[\nu(SN)/\delta(NSF)] = -0.04;$$

$$F[\nu(SF)/\delta(NSF)] = 0.02; \quad \angle(NSF) = 117°$$

Much less meaningful than these comparisons is one between OPF and ONF. For instance, $F(NF)$ in ONF is only 2.2 mdyn Å^{-1},[44] whereas $F(PF)$ in OPF has a value of 4.7 mdyn Å^{-1}, demonstrating clearly the well-known weakness of NX bonds in ONX molecules resulting from the strong ionic contribution in this bond.[61]

Working on the OPF problem we also considered different isomers, e.g., the arrangement P–O–F, as in the case of N–O–F.[62] But ab initio calculations and a normal coordinate analysis showed the ground state to have a O=P—F structure. In connection with these considerations we reexamined former experimental results on N–O–F[62] with a normal coordinate analysis. However, we found that the observed isotopic shifts ($^{16}O/^{18}O$ and $^{14}N/^{15}N$) for $\nu(OF)$ and $\delta(NOF)$ at 493 cm^{-1} and 735 cm^{-1} did not fit in with our calculated ones.[63] Hence we believe that a molecule other than NOF has to be attributed to the observed absorptions.[64]

(50) Allavena, M.; Rysnik, R.; White, D.; Calder, V.; Mann, D. E. *J. Chem. Phys.* **1969**, *50*, 3399.

(51) Khanna, V. M.; Hauge, R.; Curl, R. F., Jr.; Margrave, J. L. *J. Chem. Phys.* **1967**, *47*, 5031.

(52) This is meaningful for the first one but uncommon for the latter. Normalizing to $r(PF)$, $F(PF/\angle OPF)$ will change to a value of 0.09 mdyn Å^{-1}.

(53) All constants are normalized to the bond length of the stretching coordinate involved (mdyn Å^{-1}). ONF,[44] ONCl,[43] OPCl,[3] SO_2,[50] SiF_2,[51] NSF.[45]

(54) Downs, A. J.; Gaskill, G. P.; Saville, S. B. *Inorg. Chem.* **1982**, *21*, 3385.

(55) This is a convincing example that force constants are more sensitive than changes in bond length: $r(PO) = 145$ pm for OPF and OPCl (ab initio); $r(PO) = 144$ pm for $P(O)F_3$.[56]

(56) Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1979**, *33*, 460.

(57) Moritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem.* **1971**, *10*, 344.

(58) Morino, Y.; Kuchitsu, K.; Moritani, T. *Inorg. Chem.* **1969**, *8*, 867.

(59) Normalized with respect to both bonds.

(60) Force constants containing the deformation coordinate are normalized to the SX bond which is also involved.

(61) On the other hand, $f(NO) = 15.9$ mdyn Å^{-1} in ONF,[44] demonstrating this NO bond to be stronger than the PO bond in OPF.
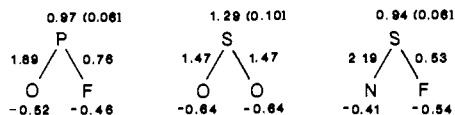
(62) Smardzewski, R. R.; Fox, W. B. *J. Am. Chem. Soc.* **1974**, *96*, 306. Smardzewski, R. R.; Fox, W. B. *J. Chem. Phys.* **1974**, *60*, 2104.

(63) These calculations have been carried out with many sets of meaningful interaction force constants as well as with a different assignment. The most suspicious disagreement was found for the $^{16}O/^{18}O$ shift of $\nu(OF)$, which has been measured to be 7.2 cm^{-1} whereas the calculated shift varies between 25 and 28 cm^{-1}.

(64) Jacox, M. E. *J. Phys. Chem.* **1983**, *87*, 4940. M. Jacox too had some doubt about the right assignment of these bands, though some of her results also favored an NOF molecule.

After comparing our results obtained experimentally with structural parameters of well-known species we get a qualitative understanding of bonding in OPF; the following quantum chemical part will describe the electronic structure of OPF in a more quantitative way.

(c) Population Analysis. The SEN (v.s. details of computations) and the atomic net charges of the isoelectronic molecules OPF, SO_2, and NSF[65] are best compared in the following scheme, which displays the atomic net charges and the SEN of respective bonds:

```
  0.97 (0.06)        1.29 (0.10)       0.94 (0.06)
      P                  S                 S
1.89/  \0.76      1.47/  \1.47      2 19/  \0.53
   O     F            O     O           N     F
 -0.52  -0.46      -0.64  -0.64       -0.41  -0.54
```

Numbers in parentheses give the hypervalent occupation,[24] which is an indicator of hypervalency, i.e., the 3d contribution which cannot be described as a polarization of 3s or 3p AOs. Hypervalent occupations of N, O, F are smaller than 0.01.

Let us first consider OPF. Roughly 0.5e electronic charge is transferred from P to O and from P to F. Together with the SEN of 1.89 (PO) and 0.76 (PF) this indicates a polar double bond P=O and a polar single bond P—F. Although F is more electronegative than O there is a slightly larger charge on O than on F, since the σ and the π bond electron pairs are polarized toward oxygen.

The present results strongly suggest that OPF has an electronic structure which is in agreement with the most simple concepts of valence considerations: O=P—F. As a consequence one expects OPF to be highly reactive since the (unprotected) polar P=O bond will very easily react as there are no further stabilizing effects. For the isoelectronic molecules SO_2 and NSF which are relatively stable species the situation is different, and actually more complicated. The electronic structure of SO_2[66] can be looked at as a resonance of

$$O=\overset{+}{S}-\overset{-}{O} \leftrightarrow \overset{-}{O}-\overset{+}{S}=O$$
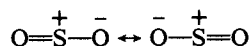
with an appreciable resonance stabilization. Since the resonance involves the valence π electrons, a more detailed picture is obtained for the MO diagram
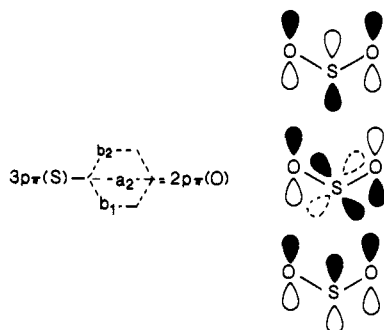
The 4-electron three-center π system leads to an accumulation of electronic charge (roughly −0.5e) at the O ligands, which is in line with the appreciable net charge $Q(O)$ = −0.64 (which includes σ and π effects). The transfer of charge from S to O lowers the 3d AOs, and one expects a pronounced $3d\pi$ contribution to the high-lying a_2 MO, which is reflected by the increased hypervalent occupation of 0.1 for S, as compared to 0.06 for P in OPF. The relative stability of SO_2 results from the π bond order of 0.7 for each SO π bond and from the $3d\pi$ stabilization of the a_2 MO. No comparable stabilizing effects are present in OPF. The stabilizing $3d\pi$ contribution to the a_2 HOMO is strongest for a linear molecule, i.e., the $3d\pi$ contribution favors larger angles. The $\angle OSO$ is in fact about 10° larger than the $\angle OPF$ in OPF.

The electronic structure of NSF is even more difficult to discuss. The SEN of the SN bond (2.19) would correspond to a strong covalent double bond, as in C_2H_4. Since the SN bond is clearly polar it is evident that there must be some triple bond character. In a previous article[67] it has been argued that the electronic structure of NSF can be considered as a resonance of

$$\overset{-}{N}=\overset{+}{S}-F \leftrightarrow N\equiv\overset{+}{S}\ \overset{-}{F}$$
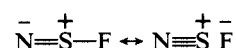
This allows the rationalization of the strength of the SN bond and the rather weak SF bond, which is indicated by a small SEN(SF) of 0.53.[68]

Conclusion

Our results on the high-temperature molecule OPF obtained by experimental and quantum chemical methods are in line with those of the well-known isoelectronic molecules SiF_2 and SO_2. Thus a detailed comparison of these small molecules with 18 valence electrons and a central atom of the third period, including the NSF species, is possible for the first time, indicating that their bonding is different from that of, e.g., the ONX species. The summary of the geometrical and the electronic structure of OPF is not unexpected and agrees well with chemical intuition.

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(65) The electronic structure of SiF_2 (two strong polar SiF bonds) is comparatively simple and clear-cut.
(66) Kutzelnigg, W. *Einführung in die Theoretische Chemie II*; Verlag Chemie: Weinheim, 1978; p 388.

(67) Zirz, C.; Ahlrichs, R. *Inorg. Chem.* **1984**, *23*, 26.
(68) This is also indicated by a weak (SF) force constant (cp. subsection: discussion of force constants).
(69) Morino, Y.; Kikuchi, Y.; Saito, S.; Hiroto, E. *J. Mol. Spectrosc.* **1964**, *13*, 95.
(70) Ehrhardt, C., Dissertation, University of Karlsruhe, 1985.
(71) In this paper the periodic group notation (in parentheses) is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)