Hyperfine Structure in the Microwave Spectrum of Trifluorophosphine Oxide and Sulfide

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The microwave spectra of $^{17}OPF_3$ and $^{33}SPF_3$ were investigated by Fourier transform microwave spectroscopy and the ^{17}O and ^{33}S quadrupole coupling constants were determined. The ^{17}O coupling constant is compared with several others from related phosphine oxides to characterize the π-bonding in these systems.

Key words: Trifluorophosphine Oxide, Trifluorophosphine Sulfide, Microwave Spectroscopy, Nuclear Quadrupole Coupling, Phosphoryl Bond

The extent of multiple bonding in phosphoryl bonds is of continuing interest; several discussions of this topic have recently been given [1–3]. We decided to measure the ^{17}O nuclear electric quadrupole hyperfine splitting (hfs) in OPF_3 using Fourier transform microwave (FTMW) techniques to add insights from nuclear quadrupole coupling constants (NQCC). The hfs from the related $^{33}SPF_3$ was also remeasured more accurately [4].

The spectra were measured in a FTMW spectrometer using a pulsed supersonic nozzle and a Fabry-Perot cavity which operates between 8–17.5 GHz [5]. About 1 atm of gas containing 98–99% Ar and 1–2% of the compound were pulsed at a rate of about 3 Hz for OPF_3 and 10 Hz for SPF_3 through a 1.0 mm orifice. Transitions were broadened ($\Delta \nu_{\mathrm{FWHM}} = 25$ kHz) by unresolved magnetic spin interactions and by Doppler effects. Line centers were determined by inspection and measured reproducibly to about 4 kHz. Line shape analysis was not undertaken because of the large number of possible components and fitting parameters which give rise to the envelope.

It was difficult to observe the $^{17}OPF_3$ species in natural abundance so a sample enriched to 3% was prepared by fluorination (SbF_3) of $^{17}OPCl_3$, prepared by hydrolyzing PCl_5 with $H_2{}^{17}O$. Only the $J = 0 \rightarrow 1$ transition was accessible with our spectrometer. The SPF_3 was prepared by heating P_4S_{10} and PbF_2. The strong $K = 0$ components of the $1 \rightarrow 2$ transition of $^{33}SPF_3$ could be seen after 10000–100000 pulses. The other $K = 0$ components and the $K = 1$ components were too weak to be measured reliably.

The observed transitions are listed in Table 1. An illustration of two components observed in $^{17}OPF_3$ is given in Figure 1. The unsplit frequencies and coupling constants were determined by linear least-squares fits. Because of the limited data set only effective B and eqQ values were determined. These are given in Table 2 and compared with other studies.

We interpreted the ^{17}O quadrupole coupling constant to estimate the extent of σ donation from phosphorus and π electron transfer from oxygen following the Townes-Dailey model as applied to triphenyl phosphate and triphenyl phosphine oxide [6]. The valence orbitals on oxygen and their orbital populations can be written as follows:

Orbital	Orbital population
$\Psi_1 = \Psi_{2p_x}$	P_{π_x}
$\Psi_2 = \Psi_{2p_y}$	P_{π_y}
$\Psi_3 = \alpha \Psi_{2s} - \sqrt{(1-\alpha^2)}\,\Psi_{2p_z}$	P_σ
$\Psi_4 = \sqrt{(1-\alpha^2)}\,\Psi_{2s} + \alpha \Psi_{2p_z}$	2

Ψ_1 and Ψ_2 are the atomic p orbitals on oxygen perpendicular to the C_3 axis, which can participate in π bonding to phosphorus. Ψ_3 is the sigma bond orbital along the P-O bond axis. Ψ_4 represents the lone pair orbital on oxygen. The quantity α^2 represents the fractional s character in the oxygen orbital used in the σ bond. Since $P_{\pi_x} = P_{\pi_y} = 2$ when there is no π back-

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donation from oxygen, the extent of π electron transfer can be defined as $4 - 2 \cdot P_{\pi_x}$.

These orbitals lead to the equation

$$q_{zz}/q_{210} = -\tfrac{1}{2}(P_{\pi_x} + P_{\pi_y}) + P_\sigma(1 - \alpha^2) + 2\alpha^2, \qquad (1)$$

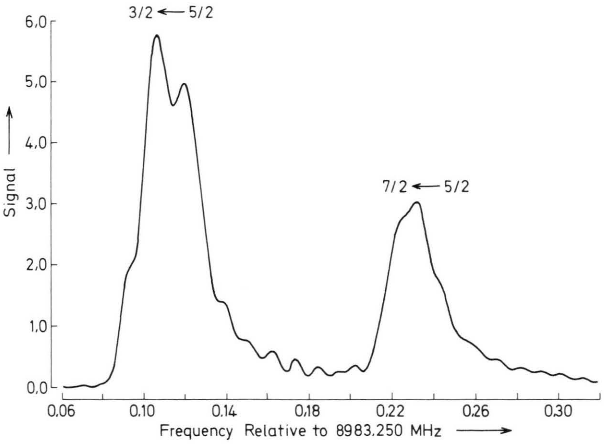

Fig. 1. Two components of the $J = 0 \rightarrow 1$ transition of $^{17}OPF_3$ (3% enriched) seen in the power spectrum. The $7/2 \leftarrow 5/2$ transition is folded over from below the origin. Sample interval 200 ns, 10 000 cycles, 1024 points supplemented by 3072 zeros.

Table 1. Measured frequencies ν_{obs} (MHz) of $^{17}OPF_3$ and $^{33}SPF_3$.

$J'-J$	K	$F'-F$	ν_{obs}	$\nu_{obs} - \nu_{calc}$	$\nu_{unsplit}$
			$^{17}OPF_3$		
1–0	0	5/2–5/2	8982.245	0.001	
		7/2–5/2	8983.023	– 0.002	8982.839
		3/2–5/2	8983.361	0.001	
			$^{33}SPF_3$		
2 1	0	3/2–1/2	10463.589	0.007	
	0	5/2–5/2	10464.215	– 0.007	
	0	1/2–1/2	10471.064	0.001	10471.063
	0	7/2–5/2	10471.702	– 0.002	
	0	3/2–3/2	10477.048	0.001	

Table 2. Rotational constants and quadrupole coupling constants of $^{17}OPF_3$ and $^{33}SPF_3$ (in MHz).

	$^{17}OPF_3$	$^{33}SPF_3$
B_{eff} [a]	4491.420(2) [b]	2617.766(2)
eqQ	–3.717(20)	–29.924(10)
B_{eff}	4491.416 [c]	2617.757(1) [d]
eqQ		–28.75(40) [d]

[a] $B_{eff} = B_0 - 2D_J$ for $^{17}OPF_3$, $B_0 - 8D_J$ for $^{33}SPF_3$.

[b] Uncertainties estimated from measurement uncertainties.

[c] Estimated from equation 2 – 33 [15] and B_0's of $^{16}OPF_3$ and $^{18}OPF_3$ [16].

[d] Ref. [4].

where q_{zz} is the experimental coupling constant and $q_{210} = 20.90$ MHz is the coupling constant for a single electron in the oxygen P_z orbital [6]. If P_{σ^0} represents the orbital population when α^2 is 0, and $P_{\pi_x} = P_{\pi_y} = P_\pi$,

$$P_{\sigma^0} = P_\sigma(1 - \alpha^2) + 2\alpha^2, \qquad (2)$$

$$q_{zz}/q_{210} = P_{\sigma^0} - P_\pi. \qquad (3)$$

Equation (3) has 2 unknowns, P_π and P_{σ^0}, containing information on the extent of σ and π bonding. Thus, only the correlation of these two quantities can be examined unless an independent estimate of one of them can be made permitting an evaluation of the other. For F_3PO, $q_{zz}/q_{210} = -0.178$ from which it is seen that $P_\pi > P_{\sigma^0}$. Cheng and Brown have pointed out that P_{σ^0} will decrease as the electronegativity (or apparent positive charge) on phosphorus increases, thus also lowering P_π and increasing the extent of π electron transfer. From a study of ^{17}O coupling data for C–O, N–O, P–O and S–O bonds they estimated that $P_{\sigma^0} \simeq 1.54$ for oxygen bonded to tetravalent phosphorus. It is interesting to use this value along with ^{17}O NQCC data to estimate the amounts of π and σ electron transfer for F_3PO, Ph_3PO [6] and $(PhO)_3PO$ [6]. This comparison is given in Table 3 for several sp hybridization values. It is clear that the π electron transfer, which is independent of the extent of sp hybridization, is sizable but about one-half to one-third as large as the phosphorus σ donation to the oxygen Ψ_3 orbital. This view of the phosphoryl bond, viz. the picture of a strong σ donation reinforced by some π back-bonding, is qualitatively in agreement with the recent analyses of H_3PO [1, 2]. Estimates of the total π-electron charge transfer in H_3PO have ranged from 0.37 to 0.58 [1, 7, 8] with the lower limit resulting from the calculation with largest basis set. Xα calculations in F_3PO [3] gave σ donation values of 1.37–1.42 e, close to P_σ estimated in Table 3; however the π donation of 0.85 to 0.89 e was considerably larger than the value obtained in Table 3.

Table 3. Estimated π- and σ-bond populations for oxygen bonded to phosphorus from a Townes-Dailey analysis.

Compound	P_{π_x}	P_{σ^0} (0% s)	P_σ (15% s)	P_σ (25% s)	π electrons transferred
F_3PO	1.72	1.54	1.45	1.39	0.56
$(PhO)_3PO$ [a]	1.73	1.54	1.45	1.39	0.55
Ph_3PO [a]	1.77	1.54	1.45	1.39	0.47

[a] Ref. [6].

It is interesting that the π electron transfer values in Table III only range over about 0.1 e. Calculations on H_2XPO species with $X = CH_3$, OH, F show a similar small spread of only 0.08 e in the back donation from oxygen. Of course it is also possible that the assumption of a constant $P_{\sigma 0}$ breaks down somewhat as the positive charge on phosphorus changes, in which case the P_π populations will vary more widely.

It is noteworthy that although the coupling constants and PO distances in F_3PO (1.437(4) Å [9]) and $(PhO)_3PO$ (1.43(1) Å [10]) are nearly the same, the stretching frequencies of 1418 cm^{-1} [11] and 1294 cm^{-1} [12] respectively are quite different. The anomalous effect of OR on the stretching frequencies in relationship to experimental bond energies was also previously recognized [1] and our study sheds little light on the origin.

Equation (3) can also be used to discuss the bonding in SPF_3. For sulfur $q_{210} = 52.00$ MHz [13] resulting in $P_{\sigma 0} - P_\pi = -0.58$. In this case the P_π population is considerably larger than P_σ implying much less π electron transfer. This correlates with comparative calculations [1] on H_3PS where the π electron back donation was about one-half that in H_3PO, and with NMR studies [14] which similarly argued for smaller contributions from π-bonding resonance structures. Since there are no other ^{33}S coupling data for thiophosphoryl compounds, it is not attractive at this time to attempt to further separate P_σ and P_π contributions using (3).

In summary, while the Townes-Dailey analysis is not unambiguous, this formalism indicates that the quadrupole coupling data for OPF_3 and SPF_3 are generally in concordance with current thought regarding the relative contributions of the σ and π bonding mechanisms to the PO and PS bonds. Perhaps of more importance, the coupling constants will provide experimental touchstones for future theoretical calculations.

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