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Fourier Transform Microwave Spectroscopic Study of Gas-Phase $ClPO_2$: Molecular Geometry and Electronic Structure Parameter Determinations

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Abstract: This paper reports the first spectroscopic study of free gas-phase $ClPO_2$. Experimental geometric parameters have been determined for the first time and insight into the electronic structure of the molecule has been gained, both from the analysis of the measured Fourier transform microwave spectra. The sample was generated inside a pulsed nozzle by passing an electric discharge through PCl_3 and O_2 in He and was subsequently stabilized in a supersonic jet expansion. The determined $ClPO_2$ parameters have been compared with those of related species.

Introduction

Phosphenic chloride, $ClPO_2$, has been studied only rarely in the past. The free, unpolymerized molecule was first detected by means of its mass spectrum[1] as one of several species produced during a high-temperature reaction between OPCl and O_2. It was subsequently produced either as a product of a photoreaction between OPCl and O_3 or as a product of a high-temperature reaction between heated Ag (1300 K), O_2, and $OPCl_3$ or PCl_3, and was isolated in a cryogenic matrix;[2] infrared spectra of three of the six fundamental vibrations and some $^{16/18}O$ and $^{35/37}Cl$ isotopic shifts of the matrix-isolated species have been recorded.[2] Simple Hartree−Fock ab initio calculations of the electronic and geometric structures have also been performed, and a partial harmonic force field analysis has been done.[2]

In this work, free gas-phase $ClPO_2$ has been prepared in an electric discharge, and pulsed jet Fourier transform microwave spectra of three isotopic species have been recorded. Hyperfine splittings due to a chlorine nuclear quadrupole interaction have been resolved. The rotational and hyperfine coupling constants determined have been used to yield geometric parameters for the molecule and to derive some information about its electronic structure; in both cases, this is the first such experimental determination of these parameters. Comparisons of these properties with the corresponding parameters of several related species are given.

Experimental Section

Transitions of $ClPO_2$ lying in the 6.8−26.2 GHz frequency range were measured using a Balle−Flygare type[3] pulsed jet Fourier transform microwave cavity spectrometer, the details of which can be found in ref 4. The samples were prepared by subjecting gas-phase sample mixtures containing roughly 1% PCl_3 and 3% O_2 diluted in 3.5 bar of He to a pulsed electric discharge immediately before expansion into the microwave cavity. A voltage of 2.5 kV was applied, and a simple 3 mm diameter straight channel nozzle extension was used; further details on the electric discharge nozzle can be found in ref 5.

Rotational transitions due to three isotopomers ($^{35}ClPO_2$, $^{37}ClPO_2$, and $^{35}ClP^{18}O^{16}O$) were observed. The mixed $^{16}O/^{18}O$ species was prepared using a 50% ^{18}O-enriched O_2 sample; this was prepared by electrolyzing (99% D; 50% ^{18}O) $D_2{}^{18}O$ that was on hand.

During automatic broadband scans and low-resolution recordings of individual transitions, 12 microwave pulses were applied to each gas pulse, and 512 data points were recorded per microwave excitation; for high-resolution measurements, only 1 microwave pulse was applied to each gas pulse, and 4096 data points were recorded. A digitizing rate of 10 MHz was used, giving a point-to-point resolution of 2.5 kHz for 4096 data points. The line frequencies were determined by analyzing the frequency domain signals,[6] and the line position uncertainties were estimated from the range of values resulting from each of several different measurements of the same transition recorded at slightly different excitation frequencies. Because the samples were injected into the cell along the cavity axis, all transitions were split into Doppler doublets (see Figure 1); the transition frequencies were obtained by averaging the two components.

Spectral Search and Analysis

During the search for high-J transitions of OPCl,[5] several transitions which could not be assigned to this molecule were found (see Figure 1). These transitions had no Zeeman splittings, thus showing that they must be due to a molecule which had no unpaired electrons, and disappeared when the electric discharge was turned off, thus showing that they were due to a species produced in the discharge. Furthermore, these transitions showed a pattern consistent with what would be expected for the hyperfine spliting of a single low-J rotational transition for a molecule containing only one Cl nucleus, and the signals disappeared when less oxygen was present in the sample mixture (in an attempt to “warm up” the molecular beam and thereby increase the intensity of the weak, high-J OPCl transition sought, the amount of oxygen used in the mixture had been increased 3-fold); the spectrum was probably due to a molecule which

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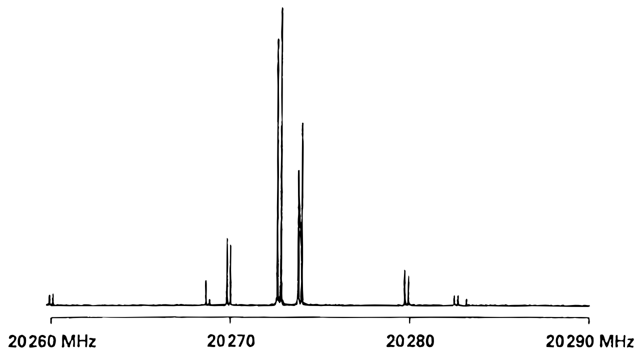

Figure 1. Overview scan in the region of 20260−20290 MHz. This spectrum is due to a molecule which is produced in the electric discharge and shows structure which is consistent with that of a low-J transition for a molecule containing a single Cl nucleus and having no unpaired electrons; it was assigned as the $3_{0,3}-2_{0,2}$ transition of $ClPO_2$. This spectrum was obtained by the concatenation of individual spectra recorded using 32 gas pulses at 12 microwave experiments per pulse; 512 data points were recorded for each microwave experiment.

contained one chlorine nucleus and more than one oxygen nucleus. Upon first consideration, only one candidate presented itself: $ClPO_2$.

A simple Hartree−Fock ab initio calculation (HF/6-31G*) of the $ClPO_2$ molecular geometry, done using the program Dalton,[7] yielded rotational constants which were not inconsistent with such an assignment: the $J_{K_a,K_c} = 3_{0,3}-2_{0,2}$ transition of the $^{35}ClP^{16}O_2$ isotopomer was predicted to lie only 200 MHz away. In addition, the hyperfine structure predicted for this transition using constants transferred from the analagous second-row species $ClNO_2$ was qualitatively consistent with what had been observed: the splittings were not correctly predicted, but the intensity pattern matched. The transitions were assigned accordingly and were put into a preliminary fit where values for the quadrupole coupling constants and the $B + C$ linear combination of rotational constants were determined; the remaining rotational constants, A and $B - C$, were held fixed to their theoretical values. Further transitions were then sought.

A scan was performed in the region of the $J_{K_a,K_c} = 2_{0,2}-1_{0,1}$ transition. This was located within 100 MHz of its predicted position; the hyperfine structure matched almost exactly with that of the new prediction. This line was included in the fit, and A was added to the list of fitted parameters. The remaining transitions were then predicted again; the $J_{K_a,K_c} = 4_{0,4}-3_{0,3}$ transition appeared within 20 MHz of this new prediction. Again, the hyperfine pattern matched almost exactly with what was predicted. The addition of this third transition in the fit then allowed for a determination of the third independent combination of rotational constants, $B - C$, and, subsequently, a much more accurate prediction of additional lines. The $J_{K_a,K_c} = 3_{2,2}-2_{2,1}$, $3_{2,1}-2_{2,0}$, and $1_{0,1}-0_{0,0}$ transitions were all found within 1 MHz of their predicted positions. Because $ClPO_2$ is a C_{2v} molecule, spin statistics dictates that levels with an odd value for K_a will be missing for all species with identical oxygen nuclei (indeed, although explicity looked for, none were found); thus, no other observable transitions (with sufficiently low J) were available within the operating frequency range of the spectrometer. A search for transitions due to the ^{37}Cl isotopomer then ensued.

Starting predictions for $^{37}ClPO_2$ were obtained by scaling the rotational constants estimated from the ab initio calculated geometric parameters by the ratio of the measured:predicted rotational constants for the normal isotopomer and by scaling the determined ^{35}Cl quadrupole coupling constants by the ratio of the ^{37}Cl and ^{35}Cl quadrupole moments; all six transitions corresponding to those already measured for the ^{35}Cl isotopomer were easily found. Transitions due to the mixed oxygen isotopomer $^{35}ClP^{16}O^{18}O$ were found using a similar procedure. In this case, however, because the two oxygen nuclei were no longer equivalent, spin statistics played no role, and many more transitions were able to be located. All measured transitions are listed in Tables 1 and 2.

At this point, high-resolution measurements of all observed transitions were made in order to try to resolve the expectedly very small spin-rotation splittings arising because of an interaction between the magnetic dipole moment of the phosphorus nucleus and the magnetic field generated by the overall rotation of the molecule. Unfortunately, while these splittings (on the order of ≈5 kHz) were clearly visible in the highest resolution spectra recorded, they were always only partially resolved, and reliable line frequencies for the two components were very difficult to determine. Ultimately, only the low-resolution spectra (where these small splittings were suppressed) were analyzed and the high-resolution data was not used except insofar as the presence of these very small splittings did offer further confirmation that the spectrum measured was indeed due to the unstable species $ClPO_2$.

All data for this prolate asymmetric molecule ($\kappa = -0.54$) were fitted under the I^r representation using Pickett's full diagonalization fitting program Spfit.[8] Rotational constants, quartic centrifugal distortion constants, and chlorine quadrupole coupling constants were used as fitting parameters; chlorine spin-rotation coupling constants were barely determined (3σ uncertainties were greater than the determined values) even when the isotopic ratios of these constants were fixed, and they were omitted from the final fits. Unfortunately, not all centrifugal distortion constants could be determined; because those which were determined in preliminary fits agreed fairly well with their theoretical harmonic force field values (within ≈2% for Δ_J of all isotopomers, for Δ_{JK} of $^{37}ClPO_2$, and for δ_J of $^{35}ClP^{16}O^{18}O$, and within ≈6% for Δ_{JK} of $^{35}ClPO_2$), all undeterminable parameters were constrained to within 10% of these predictions. The harmonic force constants and molecular geometry used were obtained from a Gaussian94[9] B3LYP/cc-pV5Z calculation, and the force field was evaluated using the program NCA.[10] The final values determined for all fitted spectroscopic constants are given in Table 3.

Discussion

1. Molecular Geometry. Up until now, very little information regarding the molecular geometry of $ClPO_2$ has been experimentally determined. From an analysis of the information obtained in an infrared investigation of the matrix-isolated species, it could be shown that the OPO bond angle was roughly 135°, and that the P−Cl bond was unexpectedly strong. Any more specific information could be obtained only from ab initio

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Table 1. Measured Transitions and Their Uncertainties, ν (MHz), and the Differences between the Observed and Calculated Frequencies, Δ (kHz), of $^{35}ClPO_2$ and $^{37}ClPO_2$

		$^{16/16}O_2P^{35}Cl$		$^{16/16}O_2P^{37}Cl$	
$J''_{K_a,K_c} - J'_{K_a,K_c}$	$F'' - F'$	ν	Δ	ν	
$1_{0,1}-0_{0,0}$	1.5−1.5	7 072.224 7(20)	−0.9	6 868.799 3(20)	0.3
	2.5−1.5	7 087.035 3(20)	2.7	6 880.472 3(20)	2.8
	0.5−1.5	7 098.884 7(20)	−2.8	6 889.809 3(20)	−2.5
$2_{0,2}-1_{0,1}$	1.5−0.5	13 894.361 2(20)	0.7	13 517.481 8(20)	1.4
	2.5−2.5	13 896.287 8(20)	−1.0	13 518.951 0(20)	−0.8
	0.5−0.5	13 908.225 0(20)	−1.0	13 528.477 3(20)	−2.3
	3.5−2.5	13 910.166 8(20)	1.6		
	2.5−1.5	13 911.097 3(20)	1.5	13 530.624 1(20)	1.8
	1.5−1.5	13 921.021 5(20)	−0.9	13 538.492 5(20)	−0.7
$3_{0,3}-2_{0,2}$	3.5−3.5	20 260.008 4(20)	−2.4	19 758.997 6(20)	−2.7
	1.5−0.5	20 268.727 3(20)	1.7		
	2.5−1.5	20 269.903 8(20)	1.5		
	4.5−3.5	20 272.725 1(20)	2.2	19 769.154 0(20)	2.4
	3.5−2.5	20 273.889 1(20)	2.0	19 770.008 0(20)	1.8
	2.5−2.5	20 279.824 9(20)	−4.0	19 774.747 9(20)	−1.6
	1.5−1.5	20 282.589 7(20)	−1.4	19 777.021 3(20)	0.4
$4_{0,4}-3_{0,3}$	2.5−1.5	26 162.609 4(20)	−1.3	25 566.938 3(20)	0.0
	3.5−2.5	26 163.628 4(20)	−0.4		
	5.5−4.5	26 164.426 0(20)	1.5		
	4.5−3.5	26 165.477 7(20)	0.3	25 569.188 7(20)	−0.1
$3_{2,2}-2_{2,1}$	3.5−2.5	21 241.390 4(20)	−0.1	20 625.840 1(20)	0.0
	2.5−1.5	21 251.952 6(20)	1.2		
	4.5−3.5	21 256.187 2(20)	−1.0		
$3_{2,1}-2_{2,0}$	3.5−2.5	22 220.301 2(20)	0.3	21 490.692 2(20)	−1.0
	2.5−1.5	22 231.194 3(20)	−3.0	21 499.266 3(20)	−0.6
	1.5−1.5	22 233.314 2(20)	−2.5		
	4.5−3.5	22 236.283 1(20)	2.8	21 503.222 6(20)	1.6
	1.5−0.5	22 247.184 7(20)	2.5		

Table 2. Measured Transitions and Their Uncertainties, ν (MHz), and the Differences between the Observed and Calculated Frequencies, Δ (kHz), of $^{35}ClP^{16}O^{18}O$

$J''_{K_a,K_c} - J'_{K_a,K_c}$	$F''-F'$	ν	Δ	$J''_{K_a,K_c} - J'_{K_a,K_c}$	$F''-F'$	ν	Δ
$1_{0,1}-0_{0,0}$	2.5−1.5	6 912.011 5(50)	2.1	$2_{1,2}-1_{1,1}$	3.5−2.5	12 448.852 1(20)	3.6
	0.5−1.5	6 923.820 0(50)	−2.5				
				$2_{1,1}-1_{1,0}$	2.5−1.5	15 179.707 6(20)	0.5
$2_{0,2}-1_{0,1}$	1.5−0.5	13 520.865 7(50)	2.2		3.5−2.5	15 194.455 6(20)	1.0
	2.5−2.5	13 522.857 8(20)	−2.8				
	0.5−0.5	13 534.572 4(20)	−0.7	$3_{1,3}-2_{1,2}$	3.5−2.5	18 504.579 5(20)	0.5
	3.5−2.5	13 536.583 3(20)	1.8		2.5−1.5	18 504.912 5(20)	−0.3
	2.5−1.5	13 537.614 9(20)	−0.2		4.5−3.5	18 507.994 5(20)	1.5
	1.5−1.5	13 547.427 9(20)	−3.1		1.5−0.5	18 508.319 2(20)	0.3
					2.5−2.5	18 508.536 8(20)	−3.2
$3_{0,3}-2_{0,2}$	2.5−1.5	19 665.656 0(100)	−1.1				
	4.5−3.5	19 668.407 0(20)	1.5	$3_{1,2}-2_{1,1}$	2.5−1.5	22 584.520 9(20)	−0.1
	3.5−2.5	19 669.632 0(20)	−0.3		3.5−2.5	22 585.381 8(20)	−0.5
					4.5−3.5	22 588.677 1(20)	1.0
$4_{0,4}-3_{0,3}$	2.5−1.5	25 324.221 0(20)	−1.5				
	3.5−2.5	25 325.215 0(20)	−0.1	$4_{1,4}-3_{1,3}$	3.5−2.5	24 419.300 0(20)	−1.7
	5.5−4.5	25 325.962 0(20)	2.0		4.5−3.5	24 419.889 0(20)	0.4
	4.5−3.5	25 327.052 0(20)	−0.6		2.5−1.5	24 420.432 0(20)	−0.3
					5.5−4.5	24 421.025 0(20)	2.0
$3_{2,2}-2_{2,1}$	3.5−2.5	20 716.398 6(100)	3.3				
	4.5−3.5	20 731.125 1(50)	−2.7	$4_{1,3}-4_{1,4}$	5.5−5.5	13 473.061 1(50)	0.2
$3_{2,1}-2_{2,0}$	3.5−2.5	21 774.511 0(100)	−2.5				
	4.5−3.5	21 790.527 3(50)	−2.7				

calculations. In this study, all geometric parameters have been experimentally determined to a fair degree of precision.

Two different types of ground-state geometries, r_0 and $r_{\Delta I/\Delta P}$, have been determined, the r_0 structure by fitting to the experimentally determined rotational constants, re-expressed in terms of the molecular or planar moments of inertia (I and P, respectively), and the $r_{\Delta I/\Delta P}$ structure by fitting to the isotopic differences in these moments. In a comparison of these two geometries, the $r_{\Delta I/\Delta P}$ parameters should be closer to the sought-after equilibrium values because, in fitting to the isotopic differences in the moments of inertia, vibrational effects will cancel to the extent that they are isotopomer independent.

The geometries were fitted using Rudolph's least-squares fitting program[11] RU111J. The rotational constants of all three

Table 3. Spectroscopic Constants of $ClPO_2$ (Uncertainties (1σ) Are Given in Parentheses)

	$^{35}Cl P^{16}O^{16}O$	$^{37}Cl P^{16}O^{16}O$	$^{35}Cl P^{16}O^{18}O$
A/MHz	8881.48(14)	8881.49(18)	8386.2045(72)
B/MHz	4225.0390(93)	4084.2866(106)	4140.8456(13)
C/MHz	2859.0313(96)	2793.8494(110)	2768.2117(10)
Δ_J/kHz	1.072(30)	0.963(37)	1.000(36)
Δ_{JK}/kHz	5.28(11)	5.33(18)	4.77(25)
Δ_K/kHz	−0.804(80)[a]	−0.546(55)[a]	−0.694(69)[a]
δ_J/kHz	0.352(35)[a]	0.326(33)[a]	0.349(18)
δ_K/kHz	4.99(50)[a]	4.81(48)[a]	4.63(41)[a,b]
χ_{aa}(Cl)/MHz	−59.2435(29)	−46.6919(34)	−59.0337(50)
χ_{bb}(Cl)/MHz	38.9499(84)	30.7083(114)	38.7592(103)
χ_{cc}(Cl)/MHz	20.2936(78)	15.9836(102)	20.2745(94)

[a] Constrained to within 10% of their theoretically predicted values (see text for details). [b] While most of the constrained constants remained virtually unchanged, δ_K of $^{35}Cl^{16}O^{18}O$ changed its value slightly (well within the 10% limit) and lowered its uncertainty somewhat (from 0.46 to 0.41 kHz); while this constant is clearly not determinable from the data, by putting limits on the other nondeterminable constants a rough "experimental" value can be found.

isotopomers studied and their correlation coefficients were used as input parameters. The data were weighted according to the inverse squares of their uncertainties. These were artificially set to be equal for all isotopomers (0.150 MHz for A and 0.01 MHz for both B and C: roughly the experimental uncertainties determined for both $^{35}ClPO_2$ and $^{37}ClPO_2$ in the spectroscopic fits) so that there was no undue emphasis placed on the $ClP^{16}O^{18}O$ data (which was more precisely determined simply because many more transitions were able to be measured for the nonsymmetric species).

Because the number of input parameters used outweighed the number of geometric parameters to be determined, many different individual fits were able to be carried out: one to all determined moments, and one each to the four different pairs (I_a and I_b), (I_a and I_c), (I_b and I_c), and (P_a and P_b) of the determined moments; fits to the other two possible pairs of molecular moments, (P_a and P_c) and (P_b and P_c), were omitted because of the planarity constraint ($P_c = 0$). For the ground-state effective (r_0) geometry determination, only the fit to I_b and I_c gave results which were not critically correlated (correlations greater than 0.999 between at least two of the three independent geometric parameters); for the vibrationally corrected ($r_{\Delta I/\Delta P}$) determinations, all five sets of results showed no critical correlations. Thus, of the two determined geometries, the $r_{\Delta I/\Delta P}$ parameters are considered to be more meaningful and more trustworthy.

The results are compiled in Table 4, where the parameter values given are those obtained by averaging the results of all five fits and the parameter uncertainties given are the standard deviation uncertainties determined during the averaging procedure (3σ). Results obtained in this manner are considered to be better than those obtained from a single fit because, by looking at the range of values resulting from fits of different combinations of data, a more realistic estimate of the parameter uncertainties can be obtained (each individual fit giving unrealistically small uncertainties because of the very good precision of the fitted data). In both cases, the uncertainties determined using this procedure look to be reasonable. Both geometries are seen to be very similar, indicating that the zero-point vibrational contributions (or at least the isotopomer independent portion thereof) are small.

A comparison of the geometric parameters of $ClPO_2$ with those of some related molecules is given in Table 5. In general, the structural parameters of $ClPO_2$ and the related $ClNO_2$ are quite similar to those of related, normally bonded molecules: for $ClPO_2$, the P═O bond length and the OPO bond angle are similar to those found in free PO_2 and the ClPO bond angle is very close to that of ClPO; for $ClNO_2$, the NO bond length and ONO and ClNO bond angles are similar to the respective parameters in NO_2 and ClNO. The Cl−P/N bond, on the other hand, is rather unusual in both cases: in $ClPO_2$ the P−Cl bond is remarkably short and strong in comparison to those of ClPO and PCl_3, and in $ClNO_2$, although the situation is not as extreme as it is in ClNO, the Cl−N bond is unusually long and weak in comparison to the "normal" N−Cl bond of NCl_3. Both the unusual shortness of the $Cl-PO_2$ bond and the distinct contrast between the $Cl-PO_2$ and $Cl-NO_2$ bonding can be explained, however, by the hypervalent character of $ClPO_2$.

$ClPO_2$ is a hypervalent molecule, whereas PCl_3, ClPO, and $ClNO_2$ are not. In $ClPO_2$, the 3d phosphorus atomic orbitals (AOs) make significant contributions to the molecular orbitals (MOs), thus allowing the possibility of $p_\pi - d_\pi$ back-bonding from the Cl to P and strengthening of the P−Cl bond.[2,12] In PCl_3 and ClPO, these same phosphorus AOs contribute very little toward the MOs, and this bond-strengthening effect is not seen;[12] for the nitrogen (second-row) compounds, there are no low-lying d orbitals and, therefore, no d-orbital contributions to the MOs that could be used to strengthen the N−Cl bond. In fact, because nitrogen (as well as all other second-row compounds) does not form hypervalent compounds,[13] the electronic structures of the second- and third-row analogues $ClNO_2$ and $ClPO_2$ are significantly different from one another and these two "related" species should not really be compared. Their geometries are not expected to show similarities.

2. Quadrupole Coupling and the Electronic Structure around the Chlorine Nucleus. Nuclear quadrupole splittings of rotational transitions result when a nuclear electric quadrupole moment (present in all nuclei with a spin $I \geq 1$) interacts with the electric field gradient surrounding that nucleus. The nuclear quadrupole coupling constants can, therefore, be used to derive information about the electronic structure around the nucleus in question.

The electric field gradient around the chlorine nucleus of $ClPO_2$ is, to a first approximation, due only to the unequal filling of the chlorine valence-shell p orbitals. The principal quadrupole coupling constants χ_{xx}, χ_{yy}, and χ_{zz} (in this case corresponding to the principal inertial axis components χ_{bb}, χ_{cc}, and χ_{aa}, respectively) can, therefore, be approximately defined in terms of the valence-shell p-orbital electron densities:[14]

$$\chi_{xx} = -\left(\frac{n_y + n_z}{2} - n_x\right) eQq_{310} \tag{1}$$

$$\chi_{yy} = -\left(\frac{n_x + n_z}{2} - n_y\right) eQq_{310} \tag{2}$$

$$\chi_{zz} = -\left(\frac{n_x + n_y}{2} - n_z\right) eQq_{310} \tag{3}$$

where n_x, n_y, and n_z are the occupations of the valence shell p_x, p_y, and p_z orbitals, respectively, and eQq_{310} is the coupling due

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Table 4. The Derived $ClPO_2$ Geometric Parameters and the Data Used in Their Determinations

	r(P=O)/Å	r(P−Cl)/Å	∠(ClPO)/deg	∠(OPO)/deg
r_0	1.450(4)	1.971(6)	113.0(5)	134.1(9)
$r_{\Delta I/\Delta P}$	1.448(2)	1.972(2)	112.9(2)	134.2(3)

	$^{35}ClP^{16}O^{16}O$	$^{37}ClP^{16}O^{16}O$	$^{35}ClP^{16}O^{18}O$
A/MHz	8881.48(15)[a]	8881.49(15)[a]	8386.2045(1500)[a]
B/MHz	4225.0390(100)[a]	4084.2866(100)[a]	4140.8456(100)[a]
C/MHz	2859.0313(100)[a]	2793.8494(100)[a]	2768.2117(100)[a]
	Correlation Coefficients		
A	1.000	1.000	1.000
B	0.973 1.000	0.978 1.000	0.187 1.000
C	−0.978 −0.997 1.000	−0.982 −0.998 1.000	−0.125 −0.908 1.000

[a] Artificially set uncertainties; for explanation, see text.

Table 5. Comparison of the Geometric Parameters of $ClPO_2$ with Those of Related Molecules

		r(P/N=O)/Å	r(P/N−Cl)/Å	∠(Cl−P/N−O)/deg	∠(O−P/N−O)/deg	ref
$ClPO_2$	$r_{\Delta I/\Delta P}$	1.448(2)	1.972(2)	112.9(2)	134.2(3)	
ClPO	$r_{\Delta I/\Delta P}$	1.4604(28)	2.0576(8)	110.00(17)		5
PCl_3	r_e		2.039(3)			17
PO_2	r_0	1.4665(41)			135.28(83)	18
PO	r_e	1.431				19
$ClNO_2$	r_s/r_0	1.198(4)	1.843(8)	114.55(4)	130.9(8)	16
ClNO[a]	r_e	1.13571(7)	1.97263(7)	113.405(3)		20
NCl_3	r_s		1.7535(20)			21
NO_2	r_e	1.19455(3)			133.851(2)	22
NO	r_e	1.151				23

[a] Two possible equilibrium geometries were determined in the ref 20 study; the parameters given in this table are those that are more consistent with a later analysis.[24]

to a single electron in an atomic 3p orbital of chlorine, tabulated values of which can be found in ref 15. Because of the traceless nature of the quadrupole coupling tensor ($\sum_{g=x,y,z}\chi_{gg} = 0$), this set of three equations must be reduced to a system of two independent equations; these are normally expressed in terms of χ_{zz} and $\chi_{xx} - \chi_{yy}$.

Upon formation of the $ClPO_2$ molecule, the chlorine nucleus accepts electron density from the phosphorus to create a σ bond, and donates some electrons back to the phosphorus nucleus in the creation of partial π bonds. Thus, the electron density in the $3p_z$ orbital of the chlorine nucleus is increased over that of the unbonded atom ($3p_z^1$) by the amount of σ electron density accepted ($n_z = 1 + \sigma$), whereas the electron densities in the $3p_x$ and $3p_y$ orbitals are decreased over that of the unbonded atom ($3p_x^2 3p_y^2$) by the amount of density that is back-donated to P ($n_x = 2 - \pi_x$; $n_y = 2 - \pi_y$). Thus, χ_{zz} and $\chi_{xx} - \chi_{yy}$ can be expressed approximately in terms of the amount of σ- and π-electrons exchanged between Cl and P upon formation of the P−Cl bond,

$$\chi_{zz} = -\left(1 - \frac{\pi_x + \pi_y}{2} - \sigma\right) eQq_{310} \tag{4}$$

$$\chi_{xx} - \chi_{yy} = \frac{3}{2}(\pi_y - \pi_x) eQq_{310} \tag{5}$$

giving a system of two equations in three unknowns, an unfortunate situation in that the total ionic character of the bond, defined as being the number of electrons gained minus those lost ($i = \sigma - \pi_x - \pi_y$), cannot be directly derived. Not all is lost, however, because some quantitative information can still be derived by solving these two equations in terms of one of the variables, chosen here to be π_x. Substituting the experimental values determined for χ_{zz} and $\chi_{xx} - \chi_{yy}$ into the above equations, one finds that $\sigma = 0.40 - \pi_x$, $\pi = \pi_y + \pi_x = 0.11 + 2\pi_x$, $i = 0.29 - 3\pi_x$. In other words, in $ClPO_2$ the phosphorus nucleus donates at most about 0.40 σ-electron to the chlorine nucleus and takes at least about 0.11 π-electron from the chlorine nucleus, and the overall ionic character of the P−Cl bond is at most about 29%.

These results can be compared with those obtained for the related species ClPO and $ClNO_2$. As was mentioned in the discussion of the molecular geometry, ClPO is different from $ClPO_2$ in that the phosphorus 3d AOs make virtually no contributions to the molecular orbitals of ClPO. For $ClNO_2$, the situation is even simpler: contributions from the d orbitals of N are precluded because there are no low-lying d orbitals available to the second-row elements. In fact, it has long been known that nitrogen cannot have more than four covalent bonds because it cannot extend its valence shell beyond an occupation of eight (see, for example, ref 13). For both of these compounds, therefore, there is virtually no orbital overlap with the in-plane $3p_x$ orbitals of the chlorine nucleus, and no possibility of back-bonding from this orbital ($\pi_x \approx 0$). With this simplification, eqs 4 and 5 can be solved directly (quadrupole coupling constants obtained from refs 5 and 16); the results are compared to those determined for $ClPO_2$ in Table 6.

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Table 6. Comparison of the Approximate Values for the Number of σ Electrons Donated to and π Electrons Taken from the Cl Nucleus upon Bonding, and a Comparison of the Overall Ionic Character, *i*, of the P/N−Cl Bond of $ClPO_2$, ClPO, and $ClNO_2$

	σ	π	*i*
$ClPO_2$	<0.40	>0.11	<29%
ClPO	≈0.64	≈0.11	≈53%
$ClNO_2$	≈0.11	≈0.06	≈5%

The comparisons between the parameters calculated for $ClPO_2$ and those calculated for $ClNO_2$ and ClPO show no surprises: the ionic characters of the N−Cl bond of $ClNO_2$ and the P−Cl bond of ClPO are much lower and higher, respectively, than the ionic character of the P−Cl bond of $ClPO_2$. In both cases, electronegativity differences mostly determine the σ-bonding characteristics, and differences in the Cl−N/P π-orbital overlaps mostly account for the differences in the π-bonding characteristics. In the $ClNO_2$/$ClPO_2$ comparison, the electronegativity difference between Cl and the NO_2 moiety is much smaller than that between Cl and the PO_2 moiety, thus allowing the Cl nucleus of $ClPO_2$ to extract much more σ-electron density away from the central nucleus than the Cl nucleus of $ClNO_2$ can, giving a much larger positive contribution to the P−Cl bond ionicity. On the other hand, even in the absence of the in-plane π-bonding contributions which are not possible for $ClNO_2$ but may be significant for $ClPO_2$, there is a much larger back-donation of π-electrons from the Cl to the central nucleus in $ClPO_2$ because of a much larger out-of-plane π-orbital overlap (probably because of the much closer size correspondence between the atomic orbitals of Cl and P than between those of Cl and N) that makes a larger negative contribution to the P−Cl bond ionicity. The magnitude of the σ contribution is much larger than that of the π contribution, and the P−Cl bond of $ClPO_2$ turns out to be much more ionic than the corresponding N−Cl bond of $ClNO_2$. In the ClPO/$ClPO_2$ comparison, both the electronegativity differences and the orbital overlap differences contribute in the same sense, making the P−Cl bond of $ClPO_2$ less ionic than the P−Cl bond of ClPO. In terms of electronegativity arguments, it is clear that PO is less electronegative than PO_2 because the addition of the second oxygen (another electronegative substituent) will take electron density away from the central phosphorus nucleus, thus giving phosphorus a greater partial positive charge and, therefore, less electron density to donate to chlorine. In terms of the orbital-overlap contributions, the situation for ClPO is clear in that there is virtually no overlap with the π_x orbitals of Cl and, therefore, no in-plane π bonding, whereas for $ClPO_2$ the 3d phosphorus AO contributions to the $ClPO_2$ MOs make in-plane π bonding possible. Although the magnitude of the π-bonding contribution to the ionic character of the P−Cl bond of $ClPO_2$ was not able to be determined in this very simple quadrupole coupling constant analysis, it is clear that there is a larger negative contribution in the case of $ClPO_2$, thus leading to a P−Cl bond with more covalent character in the case of $ClPO_2$.

The findings of both of these comparisons are in agreement with what was expected from a comparison of the molecular geometries of $ClPO_2$, $ClNO_2$, and ClPO: the fact that $ClPO_2$ had an unusually short P−Cl bond whereas $ClNO_2$ had an unusually long N−Cl bond showed that the electronic environments around the chlorine nuclei of these two molecules are very different from one another, and the unusual shortness of the P−Cl bond of $ClPO_2$ compared to that of ClPO indicated that the Cl−PO_2 bond has a strong covalent character.

Conclusion

The unstable species $ClPO_2$ has been studied in the gas phase for the first time. Fourier transform micronwave spectra of three isotopomers have been measured. An analysis of the determined spectroscopic constants has yielded ground-state effective geometric parameters and information about the ionic character of the P−Cl bond: this species is seen to have a remarkably short and strong P−Cl bond which shows a strong covalent character.

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