Spectrum of the PCl Free-radical

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A group of diffuse violet-degraded bands near 2420 Å attributed to the PCl free-radical has been observed in absorption following the isothermal flash photolysis of PCl_3. The spectrum, similar to that of SbCl,[1] has a simple vibrational structure and was not observed when PH_3 or PBr_3 were flash photolysed.

PCl_3 (Baker and Adamson) at 0·2 mm. Hg pressure with an excess of inert gas (N_2) was flash photolysed at an energy of ~1000 Joules. The electronic absorption spectrum was recorded on Ilford HP3 plate using a Hilger quartz spectrograph, model E742, with an absorption path of 50 cm. The only other molecular spectrum observed[2] in the region 2200—6600 Å was that of

$$P_2(C^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+, v'' \leqslant 7).$$

The band heads and the vibrational assignment are given in Table 1. From the observed band heads the values of ω_e, ω_eX_e for the ground electronic state (X) and the values of ω_e, ω_eX_e, and T_e for the upper electronic state (A) of PCl were calculated and are summarised in Table 2.

TABLE 1

Band heads of PCl *spectrum* (cm.$^{-1}$)

Band	ν_{vac} (obs.)	$\Delta G_{v+\frac{1}{2}}$	$\Delta^2 G_{v+1}$	ν_{vac} (calc.)
2–0	42743			
		678		
1–0	42065		−54	
		732		
0–0	41333			
		570		
0–1	40763		−7	
		563		
0–2	40200			
3–1	(42817)			42797
4–1	(43371)			43367
1–3	40378			40376

Values within parentheses are less accurate, probably ±20 cm.$^{-1}$, because of the weakness and diffuseness of the observed bands.

TABLE 2

Constants for the two electronic states of PCl (cm.$^{-1}$)

State	T_e	ω_e	ω_eX_e
A	41234	786	27
X	0	577	7/2

Though the band at 41333 cm.$^{-1}$ is the strongest of the $v'' = 0$ progression, those at 42,065 cm.$^{-1}$ and 42,743 cm.$^{-1}$ are clearly observable. The assignment of $v' = 0,1,2$ for these bands then follows from the fact that no other bands of this progression were observed to longer wavelength.

Although PCl could be produced directly in the primary process by elimination of Cl_2, it is more likely to arise by secondary photolysis or disproportionation of PCl_2. Analogous mechanisms have been suggested for NCl, NH, and PH in the flash photolysis of NCl_3,[3] NH_3,[4] and PH_3,[5] respectively. Any of these mechanisms, in addition to optical pumping, could account for the detection of vibrationally excited levels in the ground state of PCl at room temperature. However, because of the rapid decay it was not possible to prove that PCl was in vibrational disequilibrium as was the case for SbCl.[1]

This rapid decay of PCl is, at least in part, by the exothermic reaction

$$2PCl \rightarrow P_2 + Cl_2$$

as was shown by the formation of vibrationally excited P_2 ($v'' \leqslant 7$) as PCl decayed. The reaction is analogous to the formation of vibrationally excited $P_2(v'' \leqslant 7)$ from PH [5] and provides independent evidence for the presence of PCl in the system.

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