

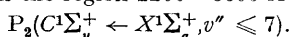
Spectrum of the PCl Free-radical

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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 PCl₃. The spectrum, similar to that of SbCl,¹ has a simple vibrational structure and was not observed when PH₃ or PBr₃ were flash photolysed.

PCl₃ (Baker and Adamson) at 0.2 mm. Hg pressure with an excess of inert gas (N₂) 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 observed² in the region 2200–6600 Å was that of



The band heads and the vibrational assignment are given in Table 1. From the observed band

and T_e for the upper electronic state (A) of PCl were calculated and are summarised in Table 2.

TABLE 2

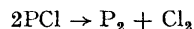
Constants for the two electronic states of PCl (cm.⁻¹)

State	T_e	ω_e	$\omega_e X_e$
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 Cl₂, it is more likely to arise by secondary photolysis or disproportionation of PCl₂. Analogous mechanisms have been suggested for NCl, NH, and PH in the flash photolysis of NCl₃,³ NH₃,⁴ and PH₃,⁵ 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



as was shown by the formation of vibrationally excited P₂ ($v'' \leq 7$) as PCl decayed. The reaction is analogous to the formation of vibrationally excited P₂ ($v'' \leq 7$) from PH⁵ and provides

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	732	-54	
0-0	41333	570		
0-1	40763	563	-7	
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.

heads the values of ω_e , $\omega_e X_e$ for the ground electronic state (X) and the values of ω_e , $\omega_e X_e$,

independent evidence for the presence of PCl in the system.

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¹ N. Basco and K. K. Yee, *Spectroscopy Letters*, 1967, in the press.

² F. Creutzberg, *Canad. J. Phys.*, 1966, **44**, 1583.

³ A. G. Briggs and R. G. W. Norrish, *Proc. Roy. Soc.*, 1964, *A*, **278**, 27.

⁴ D. Husain and R. G. W. Norrish, *Proc. Roy. Soc.*, 1963, *A*, **273**, 145.

⁵ R. G. W. Norrish and G. A. Oldershaw, *Proc. Roy. Soc.*, 1961, *A*, **262**, 1.