

Spectrum of the AsCl Free-radical

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FERGUSON and HUDES¹ have attempted unsuccessfully to observe a spectrum of AsCl in the region λ 2000—7000 by introducing AsCl₃ vapour into a stream of active nitrogen. We have observed in absorption a group of violet-degraded bands near 2450 Å following the isothermal flash photolysis of AsCl₃ which we attribute to the AsCl free-radical. The spectrum is diffuse under our resolution and similar in appearance to that of SbCl² and PCl.³ It has a simple vibrational structure and was not observed when AsH₃ or AsBr₃ were flash photolyzed.

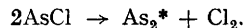
AsCl₃ (Baker & Adamson) at 0.2 mm. Hg pressure with an excess of inert gas (N₂) was flash photolyzed at an energy of ~1000 Joules. The electronic absorption spectrum was recorded on Ilford HP3 plate using a Hilger quartz spectrograph, model E742, with an absorption path of 50 cm. The spectrum of As₂(A ¹Σ_u⁺ ← X ¹Σ_g⁺, v'' ≤ 3) was also observed.⁴

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

heads the values of w_e and $w_e X_e$ for the ground electronic state of AsCl were calculated to be 443 and 2 cm.⁻¹, respectively.

Though the band at 40865 cm.⁻¹ is the stronger of the v'' = 0 progression, the band at 41385 cm.⁻¹ is clearly observable. The assignment of v' = 0,1 for these bands then follows from the fact that no other bands of this progression were observed at longer wavelength.

Although AsCl could be produced directly in the primary process by elimination of Cl₂, it is more likely to arise by secondary photolysis or disproportionation of AsCl₃. Analogous mechanisms have been suggested for NCl, NH, and PH in the flash photolysis of NCl₃,⁵ NH₃,⁶ and PH₃,⁷ respectively. Any of these mechanisms, in addition to optical pumping, could account for the detection of vibrationally excited levels in the ground state of AsCl at room temperature. However, because of the rapid decay it was not possible to prove that AsCl was in vibrational disequilibrium as was the case for SbCl.² The formation of As₂(v'' ≤ 3) as AsCl decayed can be explained by the exothermic reaction



An analogous reaction involving PH has been suggested⁷ to explain the formation of vibrationally excited P₂ in the flash photolysis of PH₃.

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TABLE

Band heads of AsCl spectrum (cm.⁻¹)

| Band | ν_{vac} | $\Delta G''_{v+\frac{1}{2}}$ | $\Delta^2 G''_{v+1}$ | $\Delta G'(\frac{1}{2})$ |
|------|--------------------|------------------------------|----------------------|--------------------------|
| 1—0 | 41385 | | | 520 |
| 0—0 | 40865 | 439 | | |
| 0—1 | 40426 | | —4 | |
| 0—2 | 39991 | 435 | | |

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⁴ G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, New York, 1950.

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⁶ D. Husain and R. G. W. Norrish, *Proc. Roy. Soc.*, 1963, **A**, 273, 145.

⁷ R. G. W. Norrish and G. A. Oldershaw, *Proc. Roy. Soc.*, 1961, **A**, 262, 1.