

Arsenic Hydride Radicals

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FLASH photolysis of arsine at ~ 20 mm. Hg pressure has yielded two new groups of sharp absorption bands which are attributed to the AsH and AsH₂ free-radicals. These assignments have been confirmed by the isotope shifts observed using fully deuterated arsine, AsD₃.

Arsine was prepared by the method described by Jolly,¹ and the deuterioarsine by the action of deuterium oxide on aluminium arsenide. The infrared spectra of the AsH₃ and AsD₃ showed negligible absorption from impurities. The electronic spectra were photographed in the first and second orders of a 21 ft. concave grating spectrograph with an absorption path of 1 metre. The

half-lives of both species under the above conditions are ~ 60 μ sec.

TABLE I. *Band heads of the ${}^3\Pi(a)-{}^3\Sigma^-$ transition of AsH and AsD (cm^{-1})*

	AsH	AsD
${}^3\Pi_0-{}^3\Sigma^-$	30,547.0	30,611.1
${}^3\Pi_1-{}^3\Sigma^-$	29,959.5	30,049.3
${}^3\Pi_2-{}^3\Sigma^-$	29,386.0	29,491.8

A group of bands near 3200 Å shows three prominent heads which are attributed to the three sub-bands of the 0-0 band of a ${}^3\Pi(a)-{}^3\Sigma^-$ transition

of AsH, by analogy with NH and PH.^{2,3} The triplet splitting is little changed on deuteration (Table 1), whereas the spacing of the rotational structure is approximately halved. For the configuration $\sigma\pi,^3\bar{I}$ the spin-orbit coupling constant, A , is minus one-half the π -orbital coefficient, so that

$$\zeta_{4p}(\text{As}) \sim 1120 \text{ cm.}^{-1}$$

The second group of bands consists of a long progression of violet-degraded bands with complex rotational structure. The band spacing decreases by $\sim\sqrt{2}$ on deuteration, and the progressions are assigned to the upper-state bending vibration of the AsH₂ and AsD₂ radicals. The isotope shifts (Table 2) lead to an unambiguous vibrational numbering, the Q -heads being represented to within $\pm 2 \text{ cm.}^{-1}$ by the equations;

$$\text{AsH}_2 \nu = 19,907.0 + 858.6 v_2 - 3.4 v_2^2$$

$$\text{AsD}_2 \nu = 19,904.9 + 618.0 v_2 - 2.1 v_2^2$$

The maximum intensities in these progressions occur at about $v_2' = 4$ for AsH₂ and $v_2' = 6$ for AsD₂, and use of the Franck-Condon principle indicates a geometry change of $\sim 30^\circ$ on excitation. This is very similar to that found for PH₂.⁴ However, the vibrational structure shows no evidence for a marked change in anharmonicity at high values of v_2' as was found in PH₂,⁵ so that the barrier to straightening the AsH₂ molecule must be considerably higher than that in PH₂.⁶ The

rotational structure of the bands near the band heads resembles closely that for PH₂,⁵ but away from the band centres there is evidence for very large doublet splittings, as would be expected from the above value of $\zeta_{4p}(\text{As})$.

The spectra are being re-photographed with longer path-lengths in high orders of a 3.4 metre Ebert spectrograph, and rotational analyses are in progress.

TABLE 2. Band heads of AsH₂ and AsD₂ (cm.⁻¹)

v_2'	AsH ₂		AsD ₂	
	ν_{vac}	ΔG	ν_{vac}	ΔG
0				
1	20,762.6			
		847.4		
2	21,610.0		21,132.2	
		844.1		606.6
3	22,451.5		21,738.8	
		835.9		603.2
4	23,287.4		22,342.0	
		828.7		600.1
5	24,116.1		22,942.1	
		819.5		597.1
6	24,935.6		23,539.2	
				590.2
7			24,129.4	
				585.8
8			24,715.2	
				580.6
9			25,295.8	

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³ F. Legay, *Canad. J. Phys.*, 1960, **38**, 797.

⁴ R. N. Dixon, G. Duxbury, and D. A. Ramsay, to be published.

⁵ D. A. Ramsay, *Nature*, 1956, **178**, 374.

⁶ R. N. Dixon, *Trans. Faraday Soc.*, 1964, **60**, 1363.