

EFFECTS OF SPIN-ORBIT COUPLING ON THE SPIN-ROTATION INTERACTION IN THE AsH<sub>2</sub> RADICAL

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The occurrence of predissociation in the electronic spectrum of AsH<sub>2</sub> is very dependent upon the magnitude of the spin-orbit coupling parameter of the central atom. Making use of Table 5.6 in "The Spectra and Dynamics of Diatomic Molecules, ELSEVIER" by H. Lefebvre-Brion and R.W. Field, it is possible to appreciate the rapid rate of increase of the spin-orbit constants associated with the heavy central atom in the di-hydrides NH<sub>2</sub>, PH<sub>2</sub> and AsH<sub>2</sub>. The spin-orbit constants range from 42.7 cm<sup>-1</sup> for NH<sub>2</sub>, to 191.3 cm<sup>-1</sup> for PH<sub>2</sub>, and 1178 cm<sup>-1</sup> for AsH<sub>2</sub>.

The effects of spin-orbit coupling may be seen in a plot of the separation of the central <sup>R</sup>Q<sub>0,9</sub> and <sup>P</sup>Q<sub>1,N</sub> sub-bands as the value of  $v_2'$  increases from 0 to 5. As the value of  $v_2'$  increases beyond 2 the spectrum becomes more and more fuzzy as the effects of predissociation become more obvious. This means that unlike the example of the behaviour of PH<sub>2</sub>, where the vibronic level pattern can be followed below and above the barrier to linearity, in AsH<sub>2</sub> and AsD<sub>2</sub> the absorption spectrum becomes completely diffuse below the barrier to linearity in the A <sup>2</sup>A<sub>1</sub> state. The change in the magnitude of the doublet splittings as  $v_2'$  increases may be seen in the plots of the doublet splittings showing the spin-uncoupling as a result of the increase of overall rotation. In the absorption spectrum of SbH<sub>2</sub>, recorded in 1967 by T. Barrow in the Chemistry Department at Sheffield University, all the absorption features showed the effects of predissociation, consistent with a spin-orbit constant of 2834 cm<sup>-1</sup> for the central atom of SbH<sub>2</sub>.