ROTATIONAL SPECTRA AND STRUCTURE OF WEAKLY BOUND $Ar(H_2S)_2$ AND $Ar(D_2S)_2$ COMPLEXES

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Rotational spectra of $Ar(H_2S)_2$ and $Ar(D_2S)_2$ complexes have been observed with a pulsed nozzle Fourier transform microwave spectrometer. About 40 a and b dipole transitions have been observed for each isotopomer. Each transition is spilt in to two as observed earlier by Lovas for the $(H_2S)_2$ complex [a]. The rotational constants for the lower state of $Ar(H_2S)_2$ are: A = 1810.410(6) MHz; B = 1596.199(9) MHz and C = 848.814(2) MHz; and those for $Ar(D_2S)_2$ are: A = 1725.49(1) MHz, B = 1566.27(3) MHz and C = 826.817(4) MHz. The C rotational constants for the two states were nearly identical, for both isotopomers. The A and B rotational constants for the upper state of $Ar(H_2S)_2$ are about 10 MHz and 6 MHz larger than those for the lower state. However, for $Ar(D_2S)_2$, A and B rotational constants for the upper state were larger only by 30 kHz and 50 kHz, respectively. This is in contrast to the very similar splittings observed in B rotational constants for $(H_2S)_2$ (1.2 MHz) and $(D_2S)_2$ (0.9 MHz). Assuming H_2S to be a sphere, the c.m. separation between two H_2S units is calculated to be 4.03 Åwhich is 0.1 Åless than that found in $(H_2S)_2$ dimer. The distance between Ar and c.m. of $(H_2S)_2$ is 3.55 Åand the Ar-c.m.(H_2S) distance is 4.09 Å. Ab initio calculations at MP2 level using various basis sets lead to three distinct minima including a pseudo-linear local minimum. At MP2/6-311++G(3df,2p) level of theory, the global minimum has a structure having Ar along the 'c' axis of $(H_2S)_2$.

[a] F. J. Lovas private communication