ROTATIONAL SPECTRUM AND STRUCTURE OF Ar_2-H_2S COMPLEX: FT MICROWAVE SPECTROSCOPIC AND AB INITIO STUDIES

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Recently there has been a great deal of interest on the second row hydrides and their weakly bonded complexes and comparison to the first row hydrides. Complexes formed by H_2O and H_2S offer a wealth of information about intermolecular interaction involving first/second row hydrides. Most of the H_2O and H_2S complexes give at least two sets of rotational transitions corresponding to different internal rotor/tunneling states. In the case of Ar-H_2S complex, an anomalous substitution effect was observed.[a] The rotational constant for Ar-D_2S was larger than that of Ar-H_2S, which is counter-intuitive. For Ar_3-H_2S, the isotope substitution effect was normal.[b] What would be the situation for Ar_2-H_2S?

Rotational transitions (asymmetric top) were predicted on the basis of an assumed geometry (C_2v). A series of *a* dipole transitions have been observed for Ar_2-$H_2{}^{32}S$. The absence of transitions between the states whose Kp and Ko are *oo* and *oe* indicates the presence of C_2 axis interchanging two identical Ar nuclei (I=0). Twenty-one transitions have been fitted to three rotational constants and five centrifugal distortion constants and these are: A=1733.0982(11), B=1617.6570(5), C=830.2755(2) MHz; d1=9.270(5), d2=25.58(2), D_J=22.20(1), D_{JK}=3.34(4) and D_K=6.17(8)kHz. The rms deviation of the fit is 2.3 kHz, which is comparable to the experimental resolution. Rotational constant A is very close to that of the free Ar_2 and this is the case in most of the Ar_2-HX complexes. Assuming H_2S to be spherical, the rotational constants are fitted to give a Ar_2(c.m.) to H_2S(c.m.) distance of 3.62 Å, and this leads to an Ar! -H_2S distance of 4.09 Å, which is comparable to the Ar-H_2S distances found in Ar_m-H_2S for m = 1 and 3. One more set of transitions has been observed and it is probably due to the ground (I = 0) internal rotor state. Further studies on this state and other isotopomers are in progress. Results will be presented in the symposium.

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[a] H. S. Gutowsky, T. I. Emilsson and E. Arunan, *J. Chem. Phys.* **106**, 5309 (1997).

[b] E. Arunan, T. I. Emilsson and H. S. Gutowsky and C. E. Dykstra, *J. Chem. Phys.* **114**, 1242 (2001).