EMPIRICAL POTENTIAL ENERGY SURFACES FOR THE $\tilde{A}\,^2\Sigma^+$ STATES OF ArSH AND KrSH

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The Bowman prescription[a] for representing the global potential for a triatomic system, A–BC, in which the BC internuclear distance is fixed, has been used to produce a good fit to high resolution rovibrational spectra for the $\tilde{A}\,^2\Sigma^+$ states of ArSH and KrSH.[b,c] Nonlinear optimization of the Bowman functional form to achieve a best rms fit between the calculated energy levels and experimental data produces a set of parameters that define the empirical potential energy surface for each system. These global surfaces have been used to predict the rovibrational energy level assignments for the HS systems as well as for the deuterium isotopes. These predicted energy levels and rotational constants are compared with all the available experimental data. While the agreement with experiment is generally very good for these systems, it is informative to consider the limitations of this approach to obtaining empirical potential energy surfaces. Specific issues to be addressed include limitations due to: (1) the assumed functional form, (2) the limited geometrical range covered by the wavefunctions associated with the experimental energy levels, (3) the assumed transferability of the potential from the HS to DS systems, and (4) the lack of coupling between the HS diatomic motion and the other internal degrees of freedom.

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a. J. M. Bowman, B. Gazdy, P. Schafer, M. C. Heaven. J. Phys. Chem **94** 2226 (1990).

b. P. P. Korambath, X. T. Wu, E. F. Hayes, C. C. Carter, and T. A. Miller Submitted to J. Chem. Phys.

c. M. -C. Yang, C. C. Carter and T. A. Miller, Submitted to J. Chem. Phys.