SIMULTANEOUS ANALYSIS OF THE Ar-SH/D COMPLEXES STUDIED BY FTMW SPECTROSCOPY

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We have previously reported a two-dimensional intermolecular potential of the Ar-SH($^2\Pi$) radical complex studied by Fourie-transform microwave (FTMW) spectroscopy [a], where only the transition frequencies of Ar-SH was used to determine the potential energy surface, although spectra were observed both for the Ar-SH and Ar-SD. In this talk, we will report a newly determined potential energy surface that is able to reproduce all the observed transition frequencies of Ar-SH and Ar-SD, simultaneously.
In the least-squares analysis, results of *ab initio* calculations, using the RCCSD(T) theory and the aug-cc-pVTZ basis set with additional bond functions located at the mid point of the vdW bond, were utilized to obtain initial values of the potential parameters. To reproduce all the transition frequencies of the two isotopomers within the experimental accuracy, the zero-point vibrations of the monomers should be considered. The effect was successfully taken into accout by introducing an additional function as an effective correction term into the term corresponding to the bond length between Ar and the center of mass of the monomer, which has the Gaussian form with its maximum at the Ar-HS configuration. The determined values for the correction term can be discussed by considering the difference of the amplitudes of the zero-point vibrations for SH and SD.

[a] Y. Sumiyoshi, Y. Ohshima, and Y. Endo, J. Chem. Phys. 113, 10121 (2000).