THE AUTOMATED CONSTRUCTION OF POTENTIAL ENERGY SURFACES SUITABLE TO DESCRIBE VDW COMPLEXES OF HIGHLY EXCITED NASCENT REACTION PRODUCT MOLECULES

ERNESTO QUINTAS SÁNCHEZ, RICHARD DAWES, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; KELVIN LEE, *Radio and Geoastronomy Division, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*; MICHAEL C McCARTHY, *Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA*.

Some reactions producing extremely hot nascent products—with vibrational quantum numbers at least as high as 30—nevertheless form relatively long-lived weakly-bound van der Waals (vdW) complexes with bath gas molecules that are observable via microwave rotational spectroscopy. One example is SiO, formed in the reaction of various silanes with oxygen.[a] The reason for the long lifetimes of the complexes, despite having internal energies that greatly exceed the vdW well depth, is the very weak coupling between the intra- and intermolecular modes. Theoretical calculations of such unbound resonance states can be much more challenging than ordinary bound state calculations since approaches to deal with the dissociating wavefunction (such as complex absorbing potentials) are less straightforward and much more time consuming. We have demonstrated that a simplified approach of making a series of vibrationally effective PESs for the intermolecular coordinates (one for each reaction product vibrational quantum number of interest) can produce vdW levels for the complex that are of spectroscopic accuracy. Here we will describe how our freely available PES fitting code called AUTOSURF[bc] can be used to construct the necessary PESs using automation. The code is demonstrated here by presenting spectroscopic-quality potential energy surfaces for Ar–CS and Ar–SiS complexes.

[a] M. C. McCarthy, S. A. Ndengué and R. Dawes, The rotational spectrum and potential energy surface of the Ar–SiO complex, J. Chem. Phys. 149, 134308 (2018).

[b] E. Quintas-Sánchez and R. Dawes, AUTOSURF: A Freely Available Program to Construct Potential Energy Surfaces, J. Chem. Inf. Model. 59, 262–271 (2019).

[c] R. Dawes and E. Quintas-Sánchez, The Construction of Ab Initio-Based Potential Energy Surfaces, Reviews in Computational Chemistry, Volume 31, Chapter 5, pp. 199-263, John Wiley & Sons (2018).