

NUMERICALLY EXACT CALCULATION OF ROVIBRATIONAL LEVELS OF $\text{Cl}^- \text{H}_2\text{O}$

XIAO-GANG WANG, TUCKER CARRINGTON, *Department of Chemistry, Queen's University, Kingston, ON, Canada.*

Large amplitude vibrations of Van der Waals clusters are important because they reveal large regions of a potential energy surface (PES). To calculate spectra of Van der Waals clusters it is common to use an adiabatic approximation. When coupling between intra- and inter-molecular coordinates is important non-adiabatic coupling cannot be neglected and it is therefore critical to develop and test theoretical methods that couple both types of coordinates. We have developed new product basis and contracted basis Lanczos methods for Van der Waals complexes and tested them by computing rovibrational energy levels of $\text{Cl}^- \text{H}_2\text{O}$. The new product basis is made of functions of the inter-monomer distance, Wigner functions that depend on Euler angles specifying the orientation of H_2O with respect to a frame attached to the inter-monomer Jacobi vector, basis functions for H_2O vibration, and Wigner functions that depend on Euler angles specifying the orientation of the inter-monomer Jacobi vector with respect to a space-fixed frame. An advantage of this product basis is that it can be used to make an efficient contracted basis by replacing the vibrational basis functions for the monomer with monomer vibrational wavefunctions. Due to weak coupling between intra- and inter-molecular coordinates, only a few tens of monomer vibrational wavefunctions are necessary. The validity of the two new methods is established by comparing energy levels with benchmark rovibrational levels obtained with polyspherical coordinates and spherical harmonic type basis functions. For all bases, product structure is exploited to calculate eigenvalues with the Lanczos algorithm.

For $\text{Cl}^- \text{H}_2\text{O}$, we are able, for the first time, to compute accurate splittings due to tunnelling between the two equivalent C_s minima. We use the PES of Rheinecker and Bowman (RB).^a Our results are in good agreement with experiment for the five fundamental bands observed.^b

^aJ. Rheinecker and J. M. Bowman, *J. Chem. Phys.* **124** 131102 (2006); J. Rheinecker and J. M. Bowman, *J. Chem. Phys.* **125** 133206 (2006)

^bS. Horvath, A. B. McCoy, B. M. Elliott, G. H. Weddle, J. R. Roscioli, and M. A. Johnson *J. Phys. Chem. A* **114** 1556 (2010)