

WEAKLY-BOUND CLUSTERS OF ATMOSPHERIC MOLECULES: THEORY AND EXPERIMENT

N. MOAZZEN-AHMADI, A.J. BARCLAY, *Department of Physics and Astronomy, University of Calgary, 2500 University Drive North West, Calgary, Alberta T2N 1N4, Canada*; **A. PIETROPOLLI CHARMET**, *Dipartimento di Scienze Molecolari e Nanosistemi, Università Cà Foscari Venezia, Via Torino 155, I-30172, Mestre, Venezia, Italy*; **A.R.W. MCKELLAR**, *National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*

Over the past decade, our group has conducted systematic investigations of infrared spectra of weakly bound dimers and larger clusters. The aim is to provide spectroscopic or dynamical observables against which high-accuracy potential energy surfaces (PESs) can be tested. As well, results on larger clusters give insight into non-additive interactions, nucleation and condensation dynamics. The fully tested PESs have wide applicability across a broader spectrum of disciplines including astrophysics, atmospheric chemistry, material sciences, and biology.

To reduce the level of complexity, we have chosen systems which are both experimentally convenient and theoretically tractable, concentrating on clusters formed from CO, N₂, CO₂, N₂O, OCS, CS₂, C₂H₂, water and rare gases. Except for those containing water, these are among the simplest systems and have a minimum number of structural parameters, essentially limited to the relative orientation of the monomers because monomer geometries are often unchanged upon complexation.

Although fully dimensional fully coupled PESs for binary complexes are now becoming more common, high level calculations on larger clusters are still scarce due to computational challenges which rise quickly with increasing cluster size. To aid our spectroscopic observations we have adopted two different strategies. First, for clusters composed of linear monomers, we perform structural cluster calculations using pair-wise additive terms from fits to ab initio PESs or from relatively simple empirical models and ignore non-additive effects. Using such structural calculations we have been able to assign rotationally resolved IR bands for medium size clusters such as (CO₂)_n, $n = 6 - 13$ and CO₂-Ar_n, $n = 3 - 17$. The second strategy involves exhaustive configurational sampling, followed by a multi-step composite approach relying on quantum calculations at increasing levels of theory where the relevant structures are refined by using double-hybrid DFT and/or CCSD(T) methods. An example of implementation of this strategy is CO-(water)_n, $n = 1 - 4$.