UCMERCED | CHEMISTRY & BIOCHEMISTRY

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CHEMISTRY & BIOCHEMISTRY SEMINAR SERIES:

Exceptionally accurate ro-vibrational energy levels and tunnelling splittings of water dimer

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Abstract:

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We have used (contracted) basis functions that incorporate coupling between inter-molecular coordinates and coupling between intra-molecular coordinates and an iterative eigensolver to compute many energy levels of water dimer (a 12-D problem). The water monomers are completely flexible. We solve the full problem in a basis of products of intramolecular and inter-molecular functions. Intra-molecular coordinates specify the shape of the monomers and intermolecular coordinates specify the relative orientation of the two monomers and distance between them. We are able, for the first time, to compute many monomer-excited states water dimer. To solve the intra-molecular and inter-molecular problems we use the Lanczos algorithm, exploiting the product structure of the primitive basis. We calculate the potential matrix for the full problem without storing the potential on a full-dimensional grid. This is done by storing an intermediate matrix, called the F matrix and parallelizing the calculation. We use a new super accurate potential energy surface computed by S. Yang and D. Zhang, who fit a two-body interaction term with a large number of high-level ab initio points. Agreement with experimental ro-vibrational spectra is extremely good. For $(H_2O)_2$ the largest error with respect to experimental inter-molecular levels up to 150 cm^{-1} is 0.58 cm^{-1}. For $(H_2O)_2$ there are few high resolution experiments that probe the intra-molecular levels. For $(D_2O)_2$, the largest error with respect to the 22 observed, out of a possible 24, experimental intra-molecular OD stretch levels up to 2800 cm^{-1} is 0.35 cm^{-1}. For $(D_2O)_2$, the largest error with respect to experimental inter-molecular levels is 0.83 cm^{-1}. The accuracy of our calculation makes it possible to re-assign several experimental bands. For the first time, we achieve the sub-cm^{-1} accuracy for water dimer ro-vibrational levels from the terahertz to the infrared.

Research:

Tucker Carrington's first academic appointment was at the University of Montreal, where he started in 1988. He received his Ph.D. in theoretical chemistry from the University of California at Berkeley. Tucker Carrington develops and applies new methods for computing rate constants, vibrational and ro-vibrational spectra, and photodisssociation cross sections. Many of the computational methods he has developed use iterative linear algebra techniques. In 2014, he won the John Polanyi award of the Canadian Society for Chemistry; in 2017, he received an Alexander von Humboldt Research Award. He was made a fellow of the Royal Society of Canada in 2023.

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