POTENTIALS, DYNAMICS, AND SPECTRA OF VAN DER WAALS AND HYDROGEN BONDED CLUSTERS

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In the first part of this lecture it will be demonstrated that accurate intermolecular potentials can be obtained from electronic structure calculations by symmetry-adapted perturbation theory (SAPT)[a], with the use of correlated monomer wave functions A recent example is Ar-CH_4 where the ab initio calculated potential surface yields very good total and state-to-state integral and differential scattering cross sections. At the same time, it yields such accurate bound state wave functions of the Ar-CH_4 complex, both in the ground and ν_3 excited state of the methane monomer, that the measured infrared spectrum could be assigned and interpreted (joint work with R. E. Miller, University of North Carolina).

The second part of this talk will focus on the tunneling motions in small water clusters. With the aid of a rigorously derived (model) Hamiltonian that includes also the overall rotation of the cluster, and the use of the permutation-inversion symmetry, we could interpret all the splittings in the measured high-resolution far-infrared spectra of $(H_2O)_3$ and $(D_2O)_3$[b]. Moreover, by means of quantitative calculations on the water dimer and trimer we could test the available water potentials, as well as a new potential from ab initio SAPT calculations[c]. New results will be presented for various water trimer isotopomers and for transitions involving vibrationally degenerate energy levels in the cyclic clusters (trimer, tetramer, and pentamer) which display unusual Coriolis coupling effects (joint work with the R. J. Saykally group, University of California at Berkeley).

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[b] A. van der Avoird, E. H. T. Olthof, and P. E. S. Wormer, *J. Chem. Phys.* **105**, 8034 (1996); E. H. T. Olthof, A. van der Avoird, P. E. S. Wormer, K. Liu, and R. J. Saykally, *J. Chem. Phys.* **105**, 8051 (1996)

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