VIBRATIONALLY AVERAGED LONG-RANGE MOLECULE-MOLECULE DISPERSION COEFFICIENTS FROM COUPLED-CLUSTER CALCULATIONS

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Recent years have seen increasing interest in the structure and dynamics of molecular clusters formed when a chromophore molecule such as CO_2, OCS or N_2O is solvated by number of He atoms and/or *para*-H_2 molecules. A key experimental probe of their behaviour is the shift of a chromophore's vibrational transition frequency which occurs when the solvent species are attached to it. Such shifts are driven by the changes in the solvent-chromophore interaction potential upon vibrational excitation of the probe molecule.[a] While 'conventional' supermolecule calculations can often provide realistic predictions of such changes in the potential well and repulsive wall region, they become increasingly unreliable for describing the weak interactions at long range where most of the solvent species in a large cluster are located. It is therefore important to have accurate relative-orientation and monomer-stretching dependent long-range C_6, C_8 and C_{10} dispersion coefficients to incorporate into the models for the interaction potential and for its dependence on the chromophore's vibrational state. This paper describes how those coefficients can be obtained from calculated monomer dipole, quadrupole, and octupole polarizabilities for imaginary frequencies, and by making use of the Casimir-Polder relation and angular momentum coupling to extract orientation-dependent quantities. The calculations are performed using a modified version of the ACES2 program system which allows the calculation of dipole, quadrupole and octupole polarizabilities at the EOM-CCSD level, and of static multipole moments using CCSD(T) calculations and adequate basis sets. For each relevant level of the chromophore, vibrational averaging is performed by calculating the imaginary frequency polarizabilities at judiciously chosen geometries and performing a numerical integration using the free-molecule vibrational wavefunction. Subsequent work will involve merging this long-range part of the potential with a short-range part obtained from 'conventional' CCSD(T) calculations and using it in PIMC simulations of cluster behaviour.

[a] H. Li, N. Blinov, P.-N. Roy and R.J. Le Roy, *J. Chem. Phys.* **130**, 144305 (2009).