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Intriguing Manifestations of Noncovalent Interactions

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Interest in noncovalent interactions has grown substantially in recent years, leading to numerous experimental and computational investigations of weakly bound dimers. Studies of their structures, dynamics, and vibrational fingerprints have revealed several intriguing—and in some cases puzzling—phenomena. This contribution focuses on such observations arising from high-level computational studies.

For weakly bound oligomers, constrained geometry optimizations are often performed, followed by harmonic vibrational analyses at geometries that are not true stationary points. A typical example is a counterpoise-corrected geometry optimization followed by a harmonic analysis that neglects the counterpoise correction. We observed[a] that extreme care is required in handling the resulting nonzero forces (this is the nonzero force dilemma[b]), as even the Hessian index can depend on the choice of coordinates in which these forces are neglected.

We have developed[c] full-dimensional potential energy surfaces for a wide range of systems involving linear triatomic molecules—neutral species such as CO_2, CS_2, N_2O, and OCS, as well as charged species including HHe_2^+, HNe_2^+, HAr_2^+, $HHeNe^+$, $HHeAr^+$, and $HNeAr^+$—solvated by a single rare-gas atom (He, Ne, or Ar). A particularly intriguing structural finding[d] is the pronounced quantum delocalization of the solvating atom.

Finally, dynamical and spectroscopic studies based on newly developed full-dimensional potential energy surfaces for the N_2[e] and CO[f] homodimers reveal additional unexpected behavior. In particular, the calculated rovibrational spectra of the N_2 dimer exhibit clear signatures of quasistructural[g] behavior.

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