UNUSUAL DYNAMICS OF LINEAR MOLECULE – RARE-GAS ATOM DIMERS

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Detailed structural, dynamical, and vibrational investigations have been carried out for van der Waals (vdW) dimers composed of linear triatomic molecular systems and a single rare-gas atom, Rg = He, Ne, and Ar [1] The chromophores of these vdW dimers include four neutral molecules, CO_2, CS_2, N_2O, and OCS, and six cations, HHe_2^+, HNe_2^+, HAr_2^+, $HHeNe^+$, $HHeAr^+$, and $HNeAr^+$, both of apolar and polar character. Electronic-structure computations reveal a peculiar exchange mechanism for the 18 formal charged complexes, of which only 12 prefer the expected T-shaped structural arrangement. For the 24 "regular" dimers, CCSD(T)-level four-dimensional (4D) PESs have been developed, keeping the two intramonomer bond lengths frozen. Employing exact kinetic-energy operators, as well as the 4D PESs and their 2D/3D cuts, first-principles nuclear-motion computations have been performed, yielding all the bound states for the 24 dimers up to the first dissociation limit. Our best models suggest that (a) the effective structures are characterized with a fully delocalized solvent Rg atom, exhibiting one or more tori around the chromophore in both the ground and the excited vibrational states, (b) certain bound states correspond to collinear molecular structures, (c) there are a few dimers for which the vdW stretch fundamental lies above the first dissociation limit, and (d) the vdW modes are almost completely decoupled from the intramonomer bending vibrations.

[1] R. Tóbiás, I. Simkó, and A. G. Császár, Unusual dynamics and spectroscopic fingerprints of van der Waals dimers formed by linear molecules and rare-gas atoms, *J. Chem. Theor. Comput.* (2023, to be submitted)