New *ab initio* results for interaction-induced dipoles and susceptibilities and new analytical results for transition probabilities

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Absorption and emission of radiation occur during collisions of H_2 with H_2, H_2 with hydrogen atoms, and H_2 with helium atoms. Our *ab initio* results for the interaction-induced dipoles of these colliding species have astrophysical applications in analysing the radiative energy balances of star-forming regions of nebula; the outer stellar atmospheres of very old, very cool white dwarf stars; and the atmospheres of the outer planets and of exoplanets classified as "hot Jupiters" and "warm Neptunes." We have computed the interaction-induced dipoles of H_2-H [1] and H_2-H_2 by finite-field methods in UCCSD(T) and CCSD(T) calculations respectively, with aug-cc-pV5Z basis sets for production runs, and aug-cc-pV6Z and d-aug-cc-pV5Z basis sets for test calculations. For H_2-H, we have determined the interaction-induced dipoles for a total of nine H_2 bond lengths, 19 angles between the H_2 bond vector and the axis from the center of mass of H_2 to the H nucleus, and 16 separations between the centers of mass of H_2 and H, for a total of 2,736 geometrical configurations [1]. For H_2-H_2, we have determined the interaction-induced dipoles for 36 pairs of H_2 bond lengths, 17 geometrical configurations, and 15 separations between the centers of mass, for a total of 9,180 geometrical configurations. A subset of the H_2-H_2 dipole values have been tested by comparison with AUTOSURF results [2] obtained by Quintas-Sanchez and Dawes at CCSD(T)-F12b/VQZ-F12 level, with excellent agreement. We have expressed the results for the dipoles as series in the spherical harmonics of the orientation angles of the H_2 molecule(s) and the intermolecular vector, to separate contributions from different polarization mechanisms and to examine the convergence to the known long-range forms. In the collision-induced dipoles of both H_2-H and H_2-H_2, we have identified the effects of static charge moments beyond the quadrupole; and for H_2-H, we have determined the long-range van der Waals dispersion contribution to the dipole for the first time in an *ab initio* supermolecule calculation on this pair. We find excellent agreement between our long-range dispersion dipole and the $D_7\,R^{-7}$ dipole computed by Bishop and Pipin using an explicitly correlated wave function for H_2 [3]. Additionally, in studies on H_2 in the ground singlet state [4] and the lowest triplet state, we have confirmed the convergence of the *ab initio* results to the known long-range analytical forms for the electrical moments and susceptibilities, through tensors of rank four. The corresponding moments and susceptibilities have also been obtained for O_2 in the ground triplet state, for use in analysing the collision-induced dipoles of O_2-O_2 in the singlet, triplet, and quintet states of the pair [5]. Recent analytical results for transition probabilities based on a separation of excited-state coefficients into their adiabatic and nonadiabatic components will also be presented [6].

References

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