Low-lying Electronic States of the Molecules AB_n (A = Sc – Ni, B = Cu/Ag/Au, n = 1,2)

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A systematic theoretical study of low-lying electronic states of the 48 molecules AB_n (A = Sc – Ni, B = Cu/Ag/Au, n = 1,2) is presented. All calculations were performed at the multi-reference configuration interaction (MRCI) level **[1,2]**, with scalar-relativistic effects included via the Douglas–Kroll–Hess approach **[3-5]**. Valence quadruple zeta basis sets were used throughout.

For the diatomic molecules AB, full and smooth potential energy curves have been calculated in the ΛS representation, wherefrom sets of spectroscopic constants (r_e, ω_e, D_e, ...) were derived. Spin-orbit coupling, core correlation effects, and basis set incompleteness have been studied for selected systems. An interesting relationship between electronic ground states of the diatomic molecules AB and of the atomic ions A^+ has been unveiled.

For the triatomic molecules AB_2, two sets of potential energy surfaces have been constructed using spline interpolation. The first set, $E(\theta_{BAB}, r_{AB;}\,{}^{2S+1}\Gamma)$, describes electronic states of the isomer BAB (linear or bent). The second set, $E(r_{AB}, r_{BB;}\,{}^{2S+1}\Lambda^{(+/-)})$, represents the linear ABB form. These are assessed, first, by considering their stabilities with respect to the asymptotes $A + B_2$, $AB + B$, and $A + 2\ B$ — all being in their respective ground states. Secondly, automatic structure optimisation was applied for the lowest state of each isomer. No overall pattern, linking all triatomic molecules AB_2 in their supposed ground states, has as yet been found — and simply may not exist.

References:

[1] MOLPRO, a package of ab initio programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others, see http://www.molpro.net. **[2]** H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, WIREs Comput. Mol. Sci. 2012, **2**, 242. **[3]** M. Douglas, N. M. Kroll, Ann. Phys. (N. Y.) 1974, **82**, 89. **[4]** G. Jansen, B. Heß, Phys. Rev. A 1989, **39**, 6016. **[5]** T. Nakajima, K. Hirao, Chem. Rev. 2012, **112**, 385.