E. Computed Structures and IR Spectra of $Co_n^+Ar_m$ Complexes

In the following, all calculated $Co_n^+Ar_m$ complexes for both PBE and PW-LDA are listed. Shown are the IR spectra together with the underlying geometry. For each structure, the spin state and the energy difference with respect to the ground-state isomer is given. All bond distances are given in units of Å. For each cluster size, the bare Co_n^+ clusters are presented first, being followed by $Co_n^+Ar_m$ complexes, which are overlapped with the IR spectra of the corresponding bare clusters to emphasize the influence of the Ar probe atom on the vibrational fingerprint. For the larger $Co_n^+Ar_m$-complexes (n=6-8), only the Co-Ar bond distances are shown for the sake of overview, since the Co-Co distances are in these cases only slightly distorted in the order of few hundreds of Å with respect to the bare cluster. For a few larger clusters, the bond distances are not explicitly given in the plot, but the atoms are labelled instead and the corresponding distances are given on the last page of this Appendix. Furthermore, the energy differences shown for the $Co_n^+Ar_m$ complexes are referred to the corresponding ground-state isomer of the $Co_n^+Ar_m$ cluster structure. Complemented are the data by the binding energy of the Ar atom and the symmetry point group, the latter being defined within a threshold of 0.01 Å. We note that in the case of the $Co_n^+Ar_m$ complexes, the symmetry point group is given for the corresponding bare cluster structure, since the Ar atom always breaks the symmetry which reduces the exact point group almost always to C_1 and thus makes the concept of the point group useless in the context of nomenclature if implying the Ar atom explicitly.

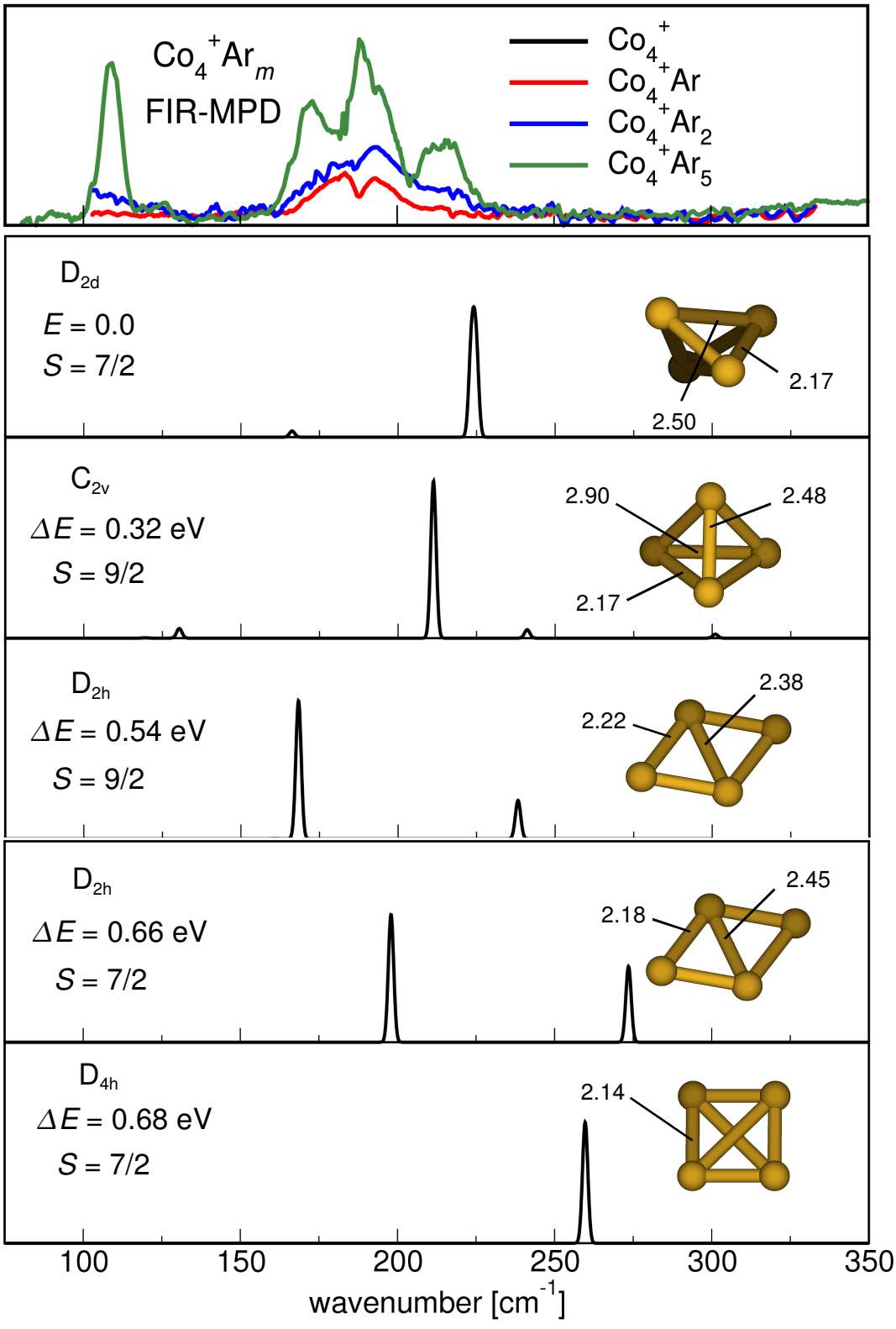

Figure E.1.: Co_4^+ IR spectra with PBE

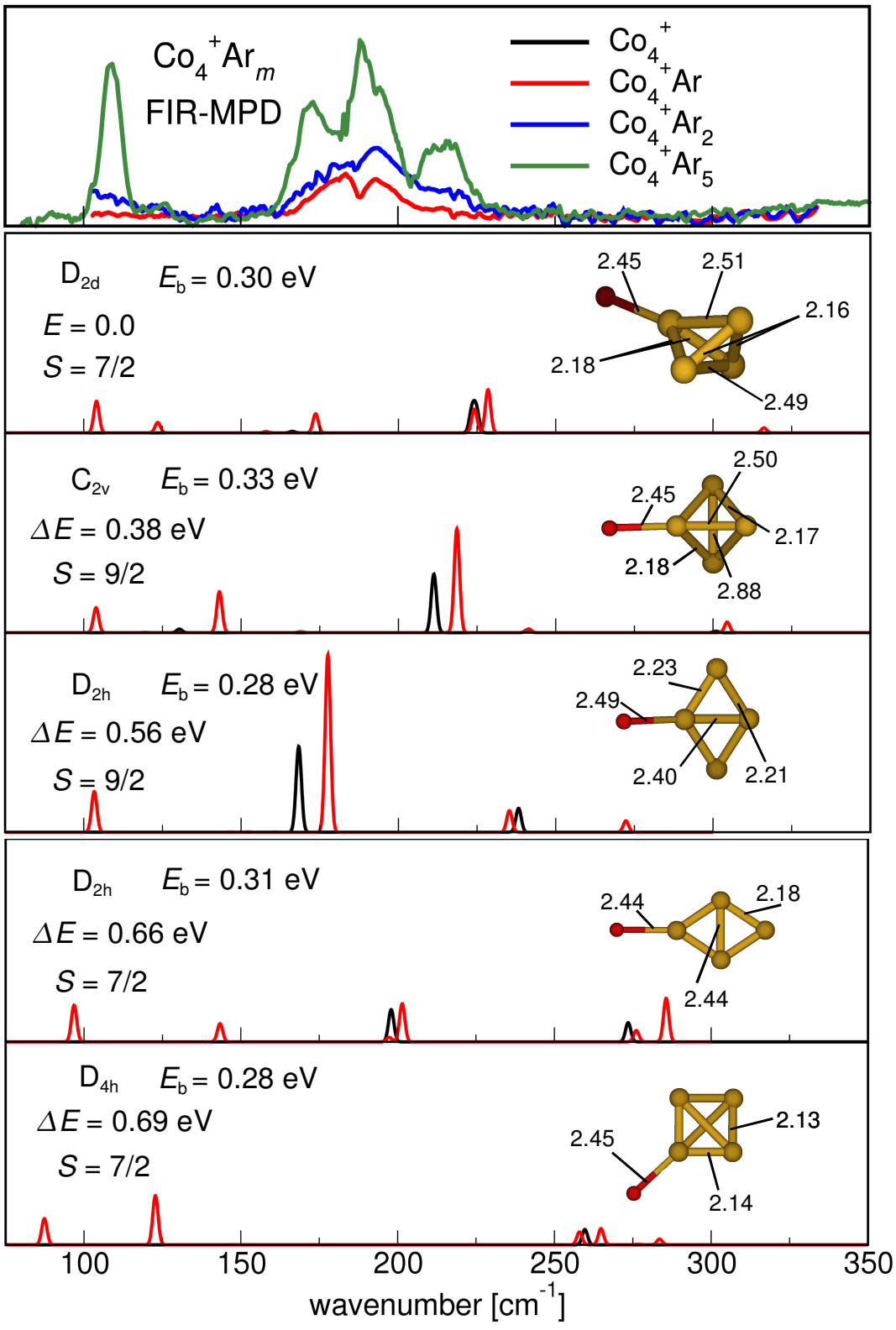

Figure E.2.: Co_4^+Ar IR spectra with PBE

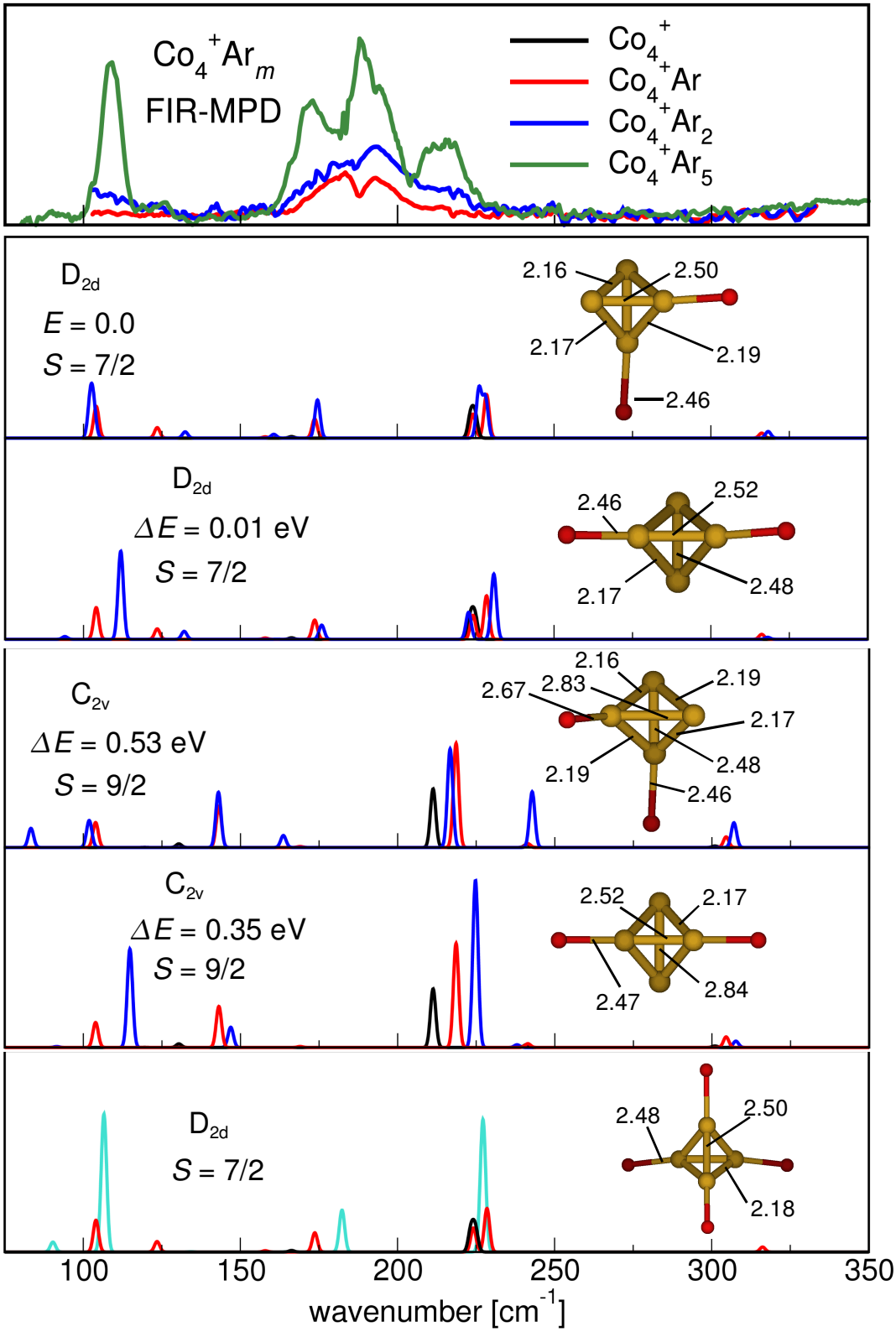

Figure E.3.: $Co_4^+Ar_m$ IR spectra with PBE

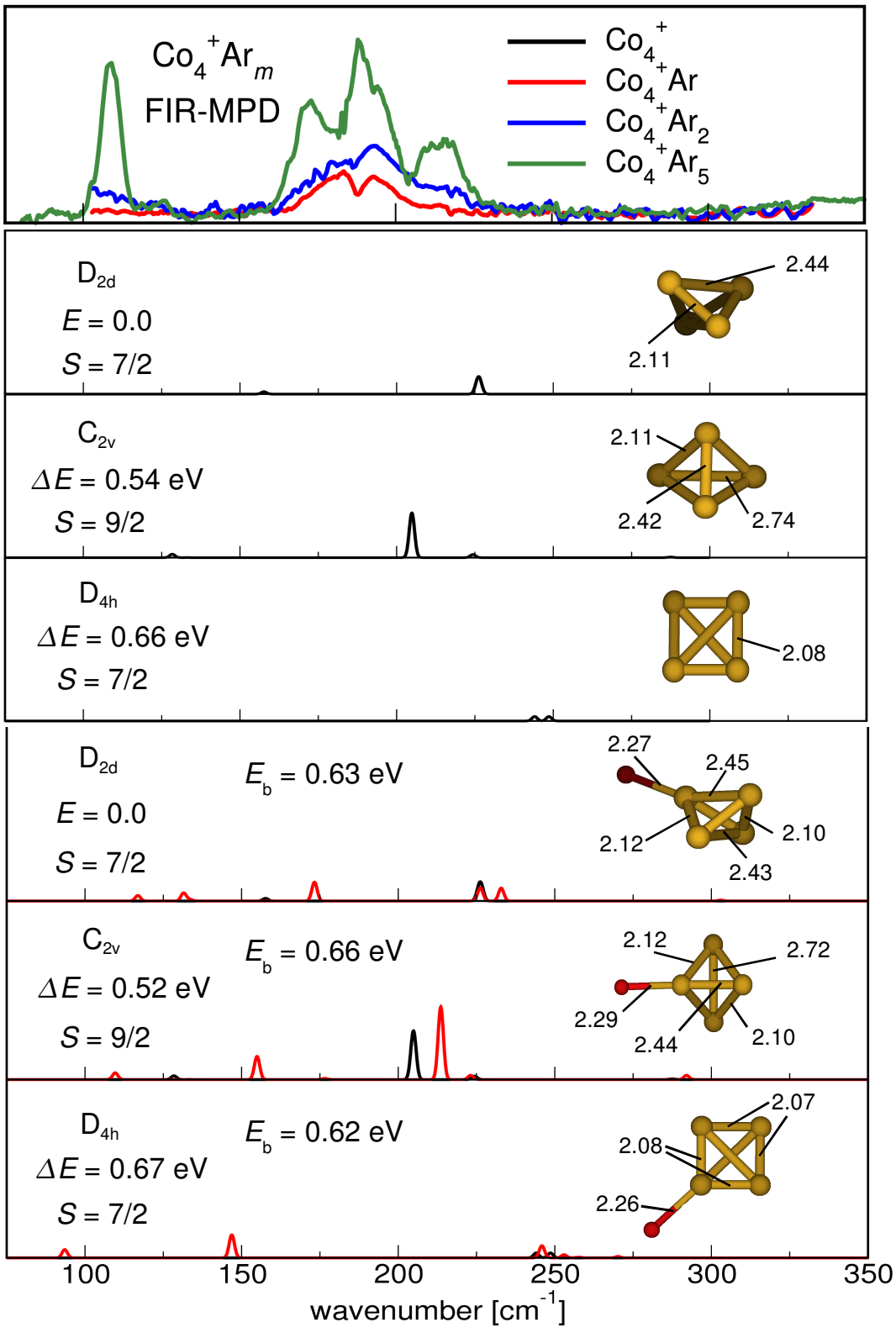

Figure E.4.: Co_4^+Ar IR spectra with PW-LDA

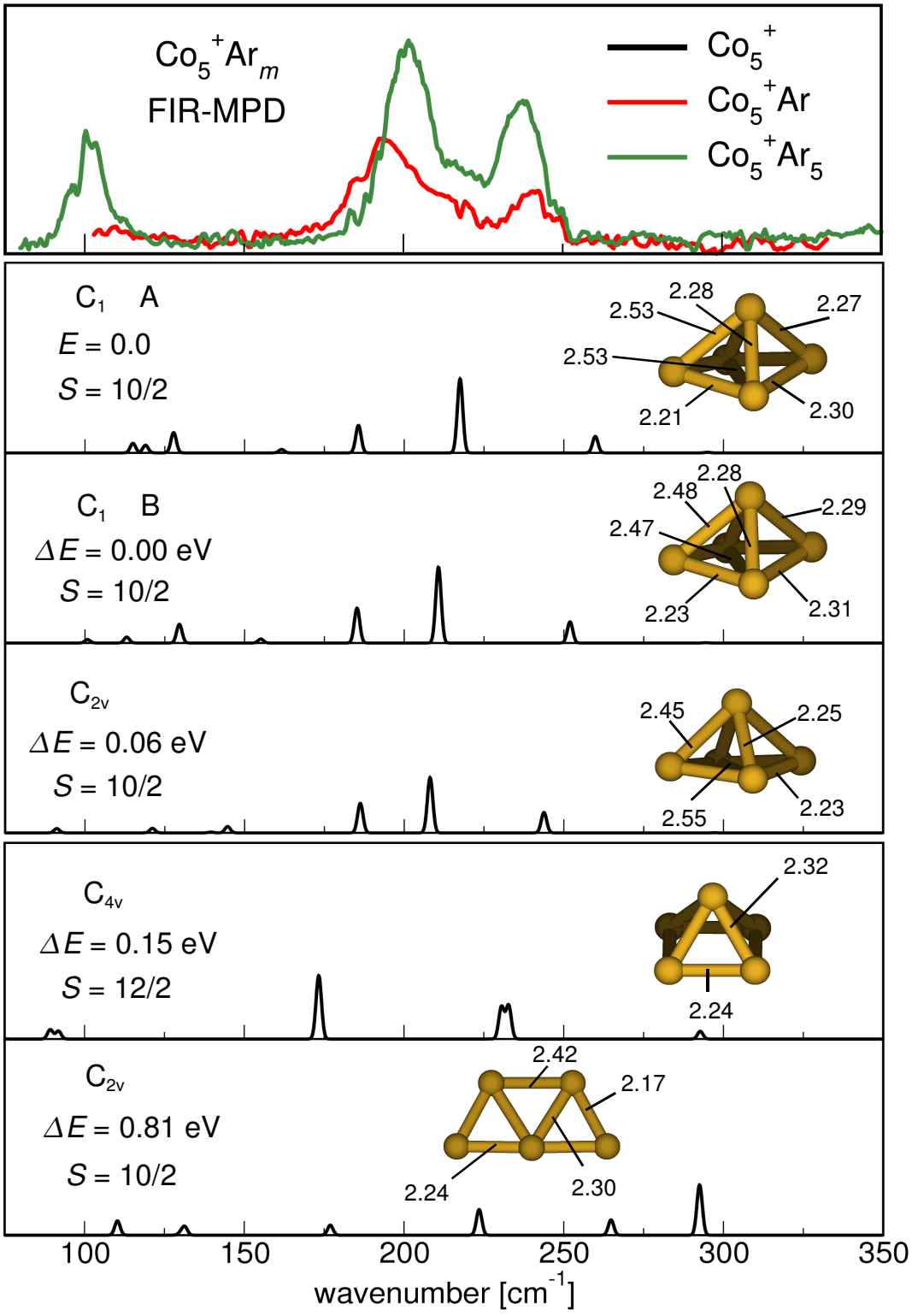

Figure E.5.: Co_5^+ IR spectra with PBE

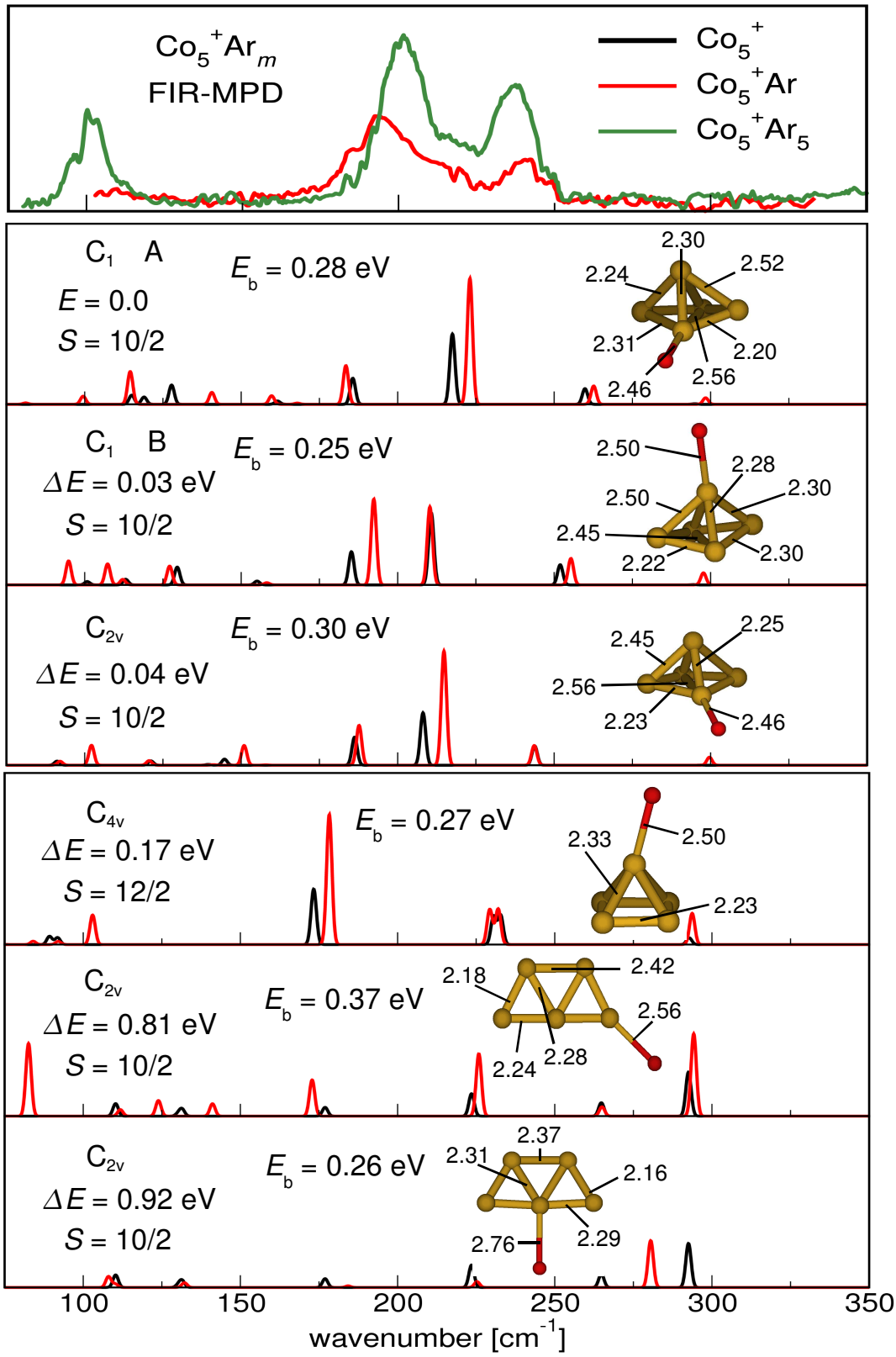

Figure E.6.: Co_5^+Ar IR spectra with PBE

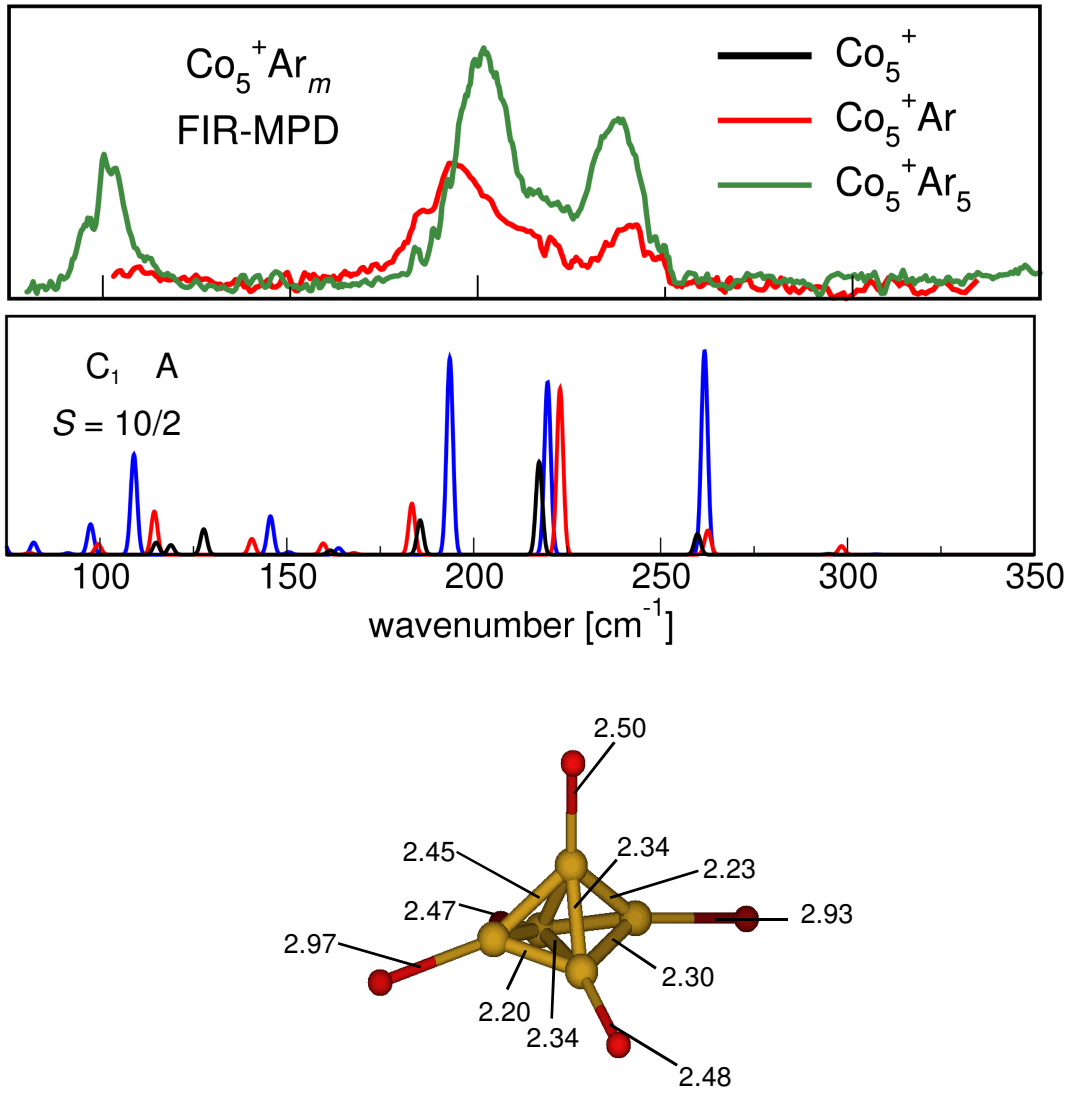

Figure E.7.: $Co_5^+Ar_5$ IR spectrum with PBE

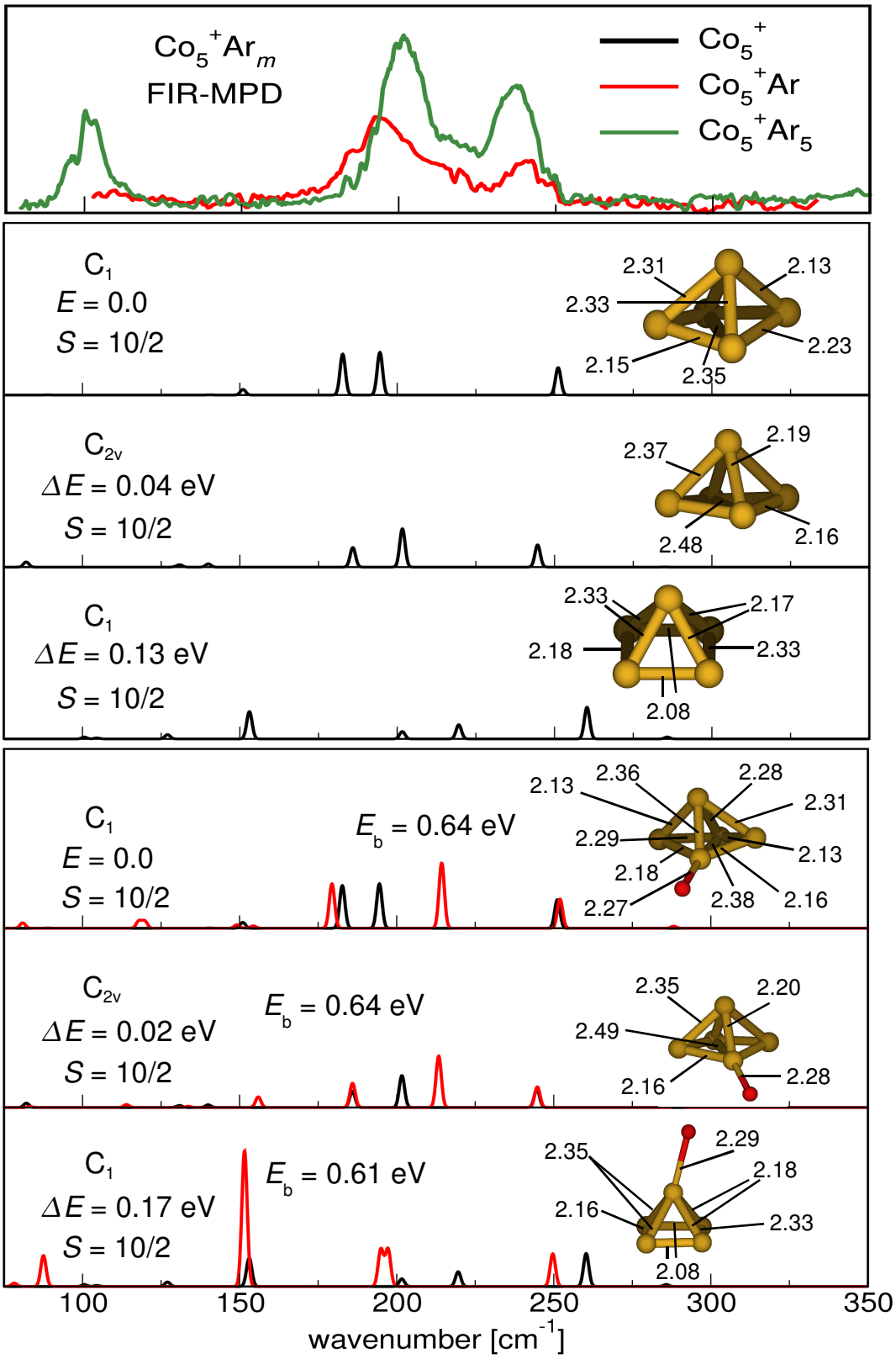

Figure E.8.: Co_5^+Ar IR spectra with PW-LDA

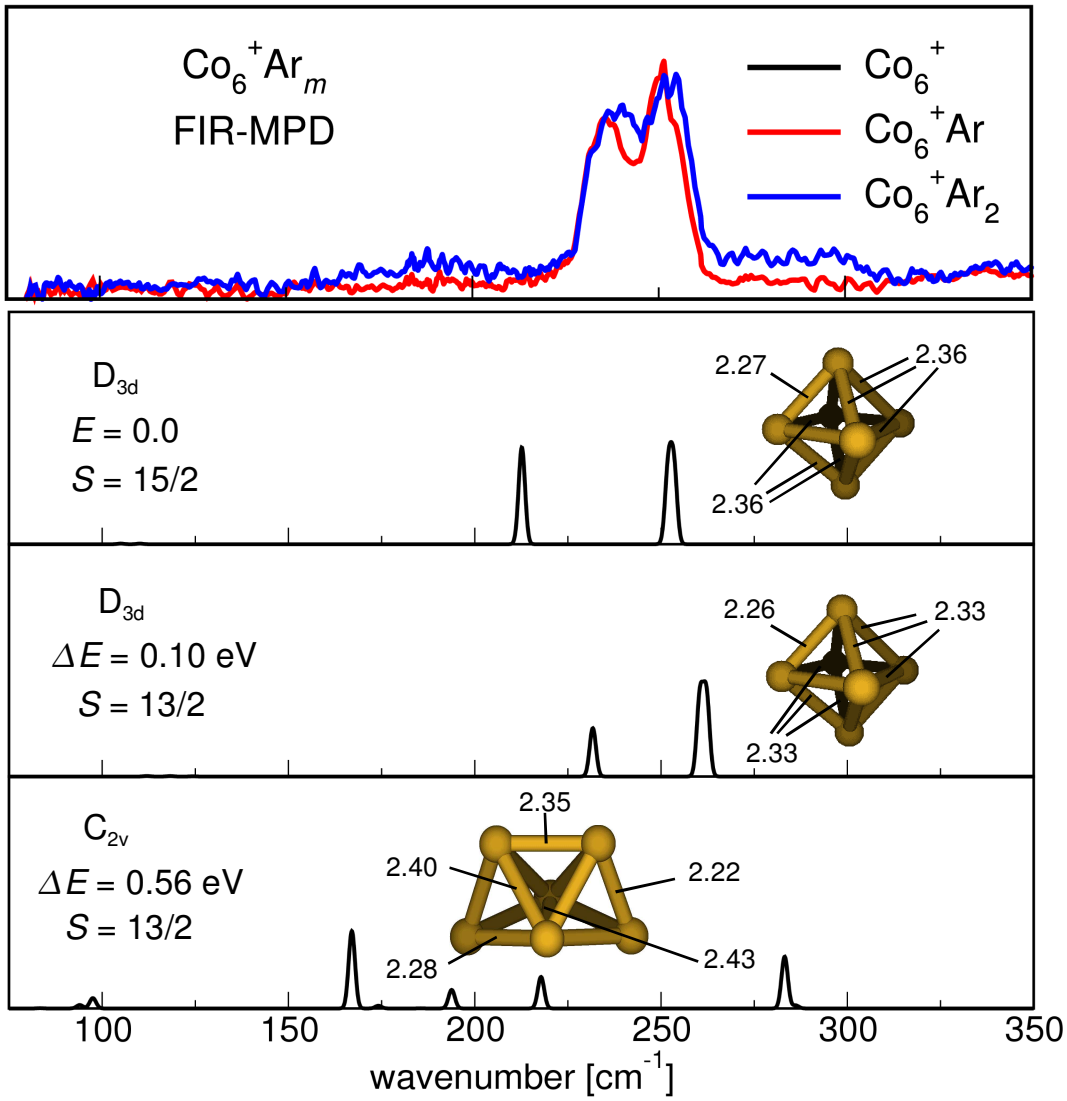

Figure E.9.: Co_6^+ IR spectra with PBE

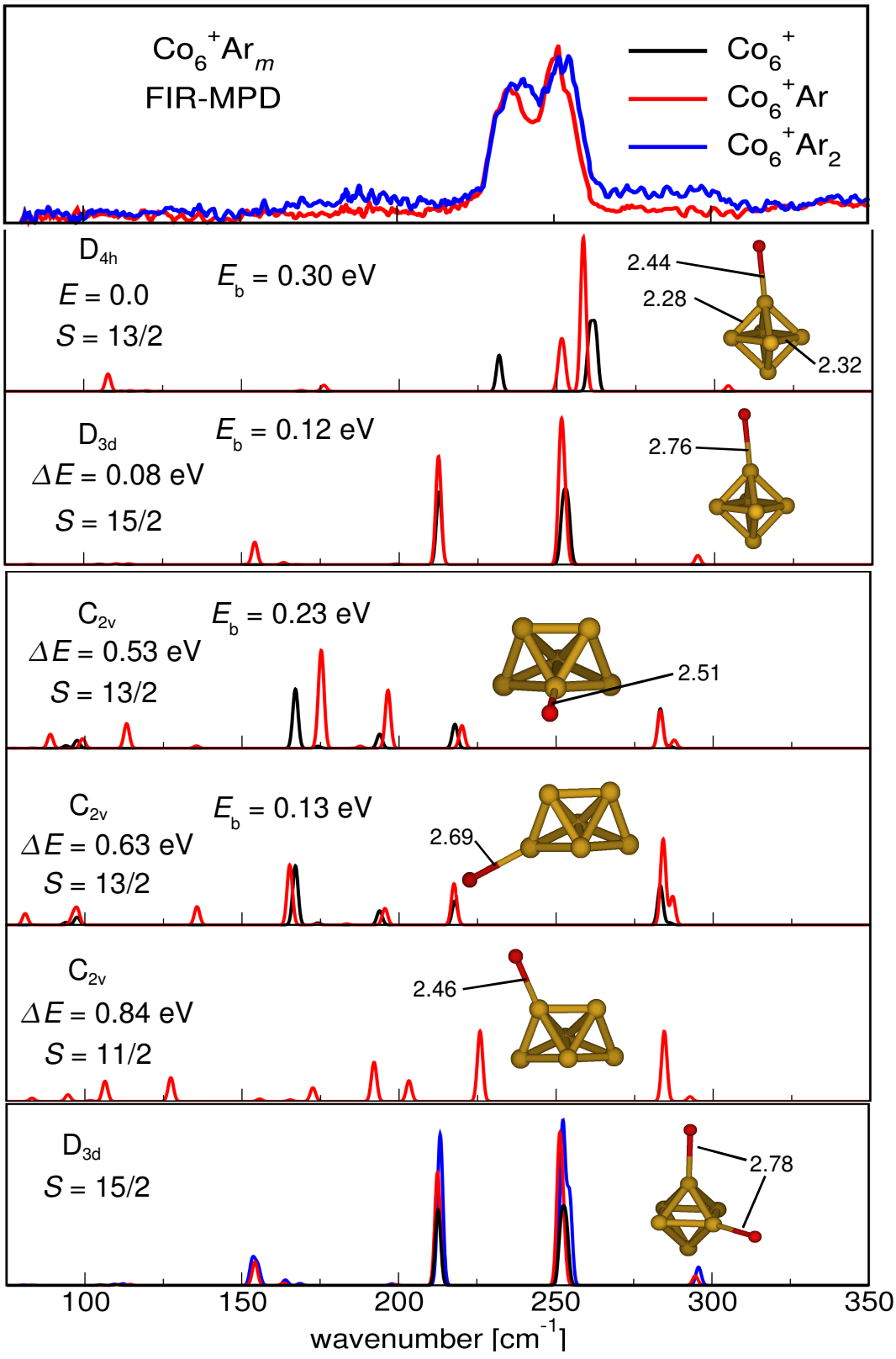

Figure E.10.: Co_6^+Ar IR spectra with PBE. We note that the S=13/2 ground-state isomer traverses a slight structural rearrangement when an Ar atom is bound and possesses D_{4h} symmetry contrary to the corresponding bare cluster with D_{3d} symmetry.

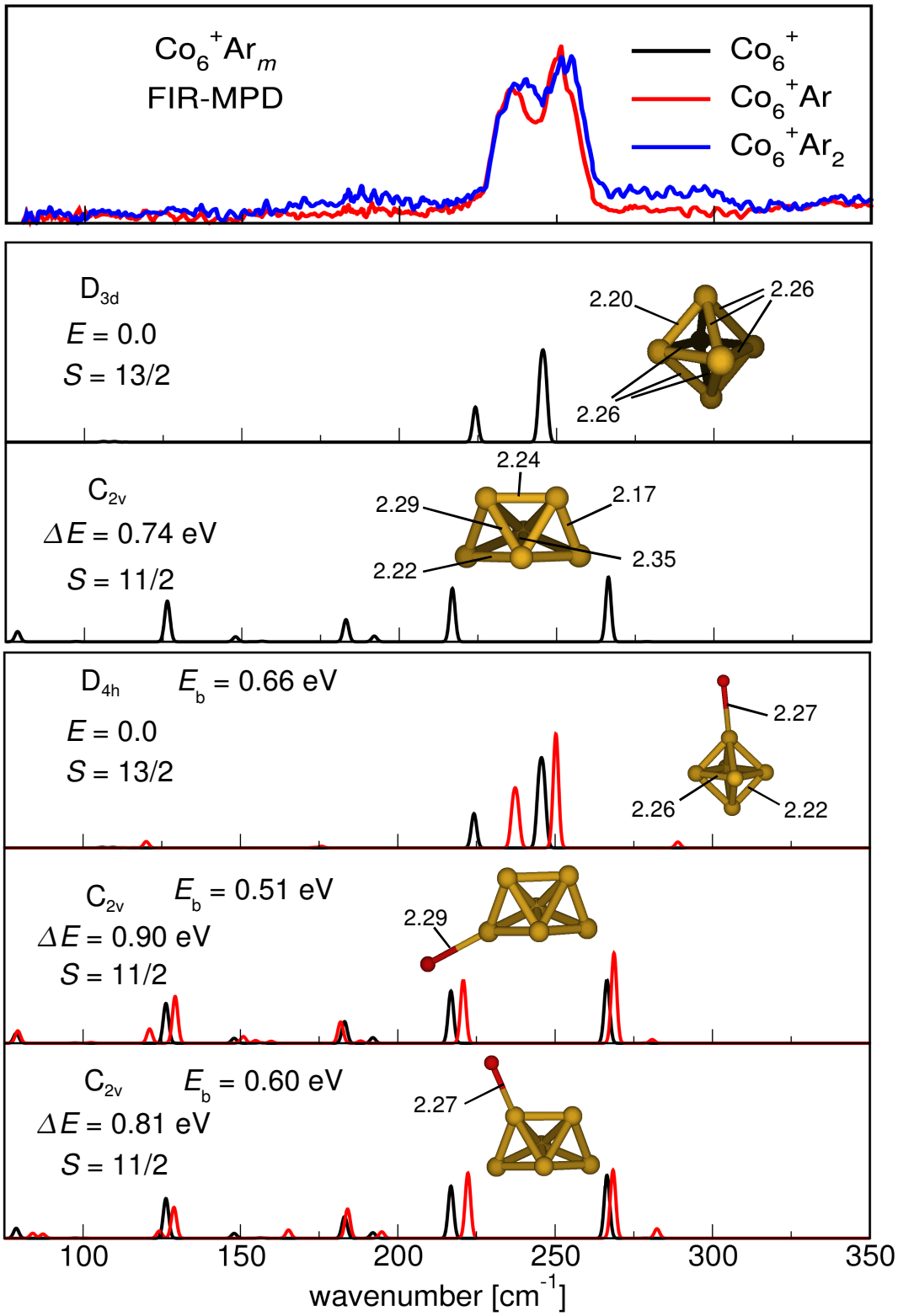

Figure E.11.: Co_6^+Ar IR spectra with PW-LDA. We note that the S=13/2 ground-state isomer traverses a slight structural rearrangement when an Ar atom is bound and possesses D_{4h} symmetry contrary to the corresponding bare cluster with D_{3d} symmetry.