ELECTRONIC STRUCTURE OF Co4(CO)12

O. V. Sizova and V. I. Baranovskii

The electronic structure of the Co4(CO)12 cluster has been studied by the extended semiempirical INDO method. The MO diagrams, atomic valences, and bond multiplicities are analyzed for the Td and C3v conformations of Co4(CO)12. Assignment of the electronic spectrum is suggested; the electronic structure of the lowest electronic-excited states is considered.

The geometrical structure of tetrametallic carbonyls M4(CO)12 in the ground state presents either an idealized tetrahedron where all ligands are terminal or a structure of C3v symmetry where the cobalt atoms lying in one of the planes are bridged by the carbonyl groups [1, 2]. The electronic structure studies of these forms are necessary for understanding the chemistry and photochemistry of these compounds. Apart from the qualitative electronic models ([3], Sec. 2 and references therein) and the general discussion based on the results of EHT studies [4, 5], the electronic structure calculations of tetrametallic carbonyl clusters were published in few papers. Using the CNDO method, Freund et al. [6] calculated and compared the MO diagrams and orbital populations for several mono- and binuclear carbonyls and two (Td and C3v) conformations of Co4(CO)12. Holland et al. [7] investigated, by the self-consistent Xα method, the effect of ligand environment on the electronic structure, spectra, and electrochemistry of Co4(CO)12 and its derivatives.

The aim of this study is to investigate and compare the electronic characteristics of different bonds in both Co4(CO)12 structures and to obtain data for the theoretical analysis of the chemistry and photochemistry of this cluster. We did not carry out geometry optimization of Co4(CO)12; instead, we fulfilled the INDO calculation for two “model” (Td and C3v) structures and for the “experimental” (C3v) geometry taken from [8, 9]. The interatomic distances are the same in both model structures: R(Co–Co) = 2.488 Å, R(Co–C) = 1.878 Å, and R(C–O) = 1.150 Å. The same bond lengths were used in the calculations of structural elements of Co4(CO)12: the metallic Co4 cluster and the CO molecule. Thus, any discrepancies in the bond indices for the model Td and C3v structures are due to the electronic factors or symmetry but not to differences in bond lengths. As an “experimental” geometry we employed the X-ray structural data of [8, 9] with bond lengths and angles averaged to provide the C3v symmetry for the molecule.* In this structure (Fig. 1), we have four types of CO groups. First, these are CO groups coordinated to the apical Co atom Coa (R(Coa–Coa) = 1.93329 Å, ∠Coa–C–Oa = 160.00°, ∠C–Coa–Coa = 101.92°). The second and third types are terminal CO groups bonded with metal atoms lying in the base of the pyramid, which include the Cob ligands lying above the base plane: the “superplanar” CO (R(Cob–Csup) = 1.9563 Å, ∠Cob–Csup–Osup = 164.87°), or below it: the “subplanar” CO (R(Cob–Csub) = 1.7393 Å, ∠Cob–Csub–Osub = 167.09°, ∠Csub–Cob–Csub = 104.40°); for these terminal groups, R(C–O) = 1.0223 Å. The fourth group is CO bridges lying in the same plane as the Cob atoms (R(Cob–Cbr) = 2.0806 Å, R(Cbr–Obr) = 1.182 Å). The bond lengths and angles cited in [8] sometimes substantially differ from the arithmetic means which we used for structural elements of the same type. Thus, R(Cob–Cbr) = 1.896-2.191 Å, R(Cob–Csup) = 1.679-2.258 Å, ∠Csup–Cob–Csub = 95.07-111.64°, ∠Cob–Csub–Osub = 162.50-177.30°.

*We thought it unreasonable to take the distorted structure determined for a crystal for the calculation of an isolated molecule.
Fig. 1. C₃ᵥ structure of Co₄(CO)₁₂ and the choice of coordinate axes.

**CALCULATION PROCEDURE**

**Method.** The limited applicability of the INDO method is largely due to the noninvariance of the calculation results with respect to rotation of the coordinate system. For molecules with a reasonably high symmetry with arbitrarily chosen coordinate axes, this also showed itself in the absence of degeneracy of molecular orbitals of e, t, or π symmetry. There are two ways to eliminate this error of the method: the averaging of all one-center interelectron repulsion integrals (in this case, the advantages of the INDO method over the less precise CNDO method are lost) and inclusion of all nonzero one-center integrals [uv | λσ]. There are relatively few such integrals: nine integrals including solely d-AO, thirty integrals including d- and p-AO, and ten integrals [sp | p'd']. Integrals of the first type may be expressed via the Slater–Condon parameters \(F^2(dd)\) and \(F^4(dd)\). The second type are \([pp' | dd'] = C \cdot F^2(pd)\) (where \(C = \pm 2 \cdot \sqrt{3}, \sqrt{3}, \pm 3\)) and \([pd | p'd'] = a \cdot G^1(pd) + b \cdot G^3(pd)\). The third type is \([sp | p'd'] = C \cdot R^1(sppd)\), where \(C = \sqrt{3}, 2, -1\) and \(R^1(sppd) = \int \int_0^∞ R_{3d}(\xi) R_{4p} (\xi') \frac{r}{r_0^2} R_{4p} (\xi') \frac{r^2}{r_2^2} dr_1 dr_2\) \((R_{nZ}(r)\) are the radial functions of the 4s-, 4p-, and 3d-AO). In contrast to the \(F^k\) and \(G^k\) parameters, the \(R^1(sppd)\) integrals are not included in the energy relations for the atomic and ionic terms [25] and, hence, may not be estimated from the atomic spectra.

We rejected calculating the one-center integrals [uv | λσ] in the analytical form because we failed to select radial functions for the 4s-, 4p-, and 3d-AO which would give an acceptable correlation with all experimentally estimated \(F^k\) and \(G^k\). Thus, for the cobalt atom, satisfactory \(F^2(dd)\) and \(F^4(dd)\) values may be obtained with the one-exponential function \(R_{3d}(2.32); F^0(dd)\), with \(R_{3d}(2.138)\); and \(F^0(ss)\), with \(R_{4d}(1.77)\). Using these functions to calculate \(F^0(sd)\) gives a good result, while for \(G^2(sd)\) we get a nearly four-fold exaggerated value. The case is similar when we calculate the integrals involving p-AO.

To assess the effect of \(R^1(sppd)\) inclusion on the results of INDO calculations, we carried out a series of calculations where \(R^1(sppd)\) for the Co atom was varied from 1 to 3.5 eV (the limiting values corresponding to realistic radial functions). The test calculations for Co(CO)₄ and Co₄ showed that inclusion of these integrals does not improve the results from the viewpoint of their invariance and the presence of degeneracy. Therefore, for an extension of the INDO method, we included only 39 additional one-center integrals involving d- and p-AO. The [sp | p'd'] integrals were left out because they may not be estimated from spectroscopic data, their calculation in the analytical form is not compatible with the empirical nature of other parameters, and their role in correcting the noninvariance of the INDO method is negligible. We note that a similar extension of the INDO method was used earlier in [10].

To calculate the excited states we employed the configuration interaction (CI) method. In the CI calculation, the wave function of the Qth state is of the form

\[ \Psi_Q = \sum_{i→j,Q} A_{i→j,Q} \Phi_{i→j}. \]