FCO_2 under the KDC model Hamiltonian

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Both qualitative description and quantitative determination of vibronic couplings inside the FCO_2 radical have been performed. The vibronic effects on the ground and the first excited state vibrational levels have been studied. The four lowest electronic states have electronic configurations and energy separations calculated by EOMIP-CCSD:

$$\begin{array}{lll}
\ldots(4b_2)^2(2b_1)^1(8a_1)^2(1a_2)^2(5b_2)^2 & \tilde{\mathrm{C}}\ {}^2B_1 & T_e \approx 3.68\,\mathrm{eV} \\
\ldots(4b_2)^2(2b_1)^2(8a_1)^1(1a_2)^2(5b_2)^2 & \tilde{\mathrm{B}}\ {}^2A_1 & T_e \approx 1.71\,\mathrm{eV} \\
\ldots(4b_2)^2(2b_1)^2(8a_1)^2(1a_2)^1(5b_2)^2 & \tilde{\mathrm{A}}\ {}^2A_2 & T_e \approx 0.65\,\mathrm{eV} \\
\ldots(4b_2)^2(2b_1)^2(8a_1)^2(1a_2)^2(5b_2)^1 & \tilde{\mathrm{X}}\ {}^2B_2 & T_e = 0\,\mathrm{eV}
\end{array}$$

The schematic 4×4 potential energy matrix for interstate interactions of the four lowest electronic states can be written as:

$$W = \begin{pmatrix}
V_X & PJT_{XA}(q_4) & PJT_{XB}(q_5, q_6) & 0 \\
PJT_{XA}(q_4) & V_A & 0 & PJT_{AC}(q_5, q_6) \\
PJT_{XB}(q_5, q_6) & 0 & V_B & PJT_{BC}(q_4) \\
0 & PJT_{AC}(q_5, q_6) & PJT_{BC}(q_4) & V_C
\end{pmatrix}$$

The intrastate and interstate coupling constants have been determined within four different approaches in the framework of the Köppler, Domcke and Cederbaum (KDC) model of vibronic Hamiltonian - adiabatic quadratic (AP2), adiabatic quartic (AP4), vertical quadratic (VP2), and vertical quartic (VP4). All *ab initio* calculations (optimization, potential energies, first and second derivatives) have been proceed in the EOMIP-CCSD method. The quartic coupling constants were determined from numerical fits. The inclusion of the vibronic couplings makes crucial changes in the potential surface for the ground state where the one-minimum quadratic shape is changed to the double-minimum along the q_5 anion normal coordinate displacement. The determined vibronical levels up to 2000 cm^{-1} are in very good agreement with the experimental spectra. For instance, AP4 provides $\nu_5 = 1122.7$ cm^{-1} which can be compared to the experimental value 1116.5 cm^{-1}.