

Jahn–Teller, pseudo-Jahn–Teller, and spin-orbit coupling effects in cerium trihalide molecules

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Low-lying spin-orbit states of cerium trihalide molecules CeX_3 ($X = \text{F, Cl, Br, I}$) are studied using single-reference CCSD(T) and multireference MRCI and MRPT2 methods with the basis sets of quadruple- ζ quality. Scalar relativistic effects are incorporated in all-electron calculations using Douglas–Kroll–Hess Hamiltonian. Spin–orbit coupling is treated either with the Breit–Pauli spin-orbit operator \hat{H}_{SO} or with spin–orbit pseudopotentials. The spin-orbit eigenstates are obtained by diagonalizing $\hat{H}_{el} + \hat{H}_{SO}$ in a basis of eigenfunctions of \hat{H}_{el} .

The originally degenerate 4f-orbitals of Ce^{3+} split into $a_2'', e', e'', a_1', a_2'$ orbitals in the ligand field of D_{3h} symmetry. The energy difference of the highest and lowest CeX_3 electronic states corresponding to different f electron occupation of these orbitals amounts to 2200, 1400, 1300, and 1100 cm^{-1} for $X = \text{F, Cl, Br, I}$, respectively, with the first excited state ${}^2E'$ lying above the ground state ${}^2A_2''$ by 100, 40, 20, 10 cm^{-1} . An accounting for spin-orbit coupling of the states changes this pattern dramatically. The energy splitting grows to 4000, 3400, 3200, and 3100 cm^{-1} . The relative energy of the first excited spin-orbit state ${}^2E_{3/2}$ with respect to the ground state ${}^2E_{5/2}$ amounts to 370 – 470 cm^{-1} .

The Jahn–Teller (JT) and pseudo-Jahn–Teller (PJT) effects are studied in detail for CeF_3 . The JT distortion ($D_{3h} \rightarrow C_{2v}$) in the ${}^2E'$ state yields the Y-shaped structure with $\alpha_e(\text{F-Ce-F}) = 115^\circ$ and the JT stabilization energy $E_{JT} = 75 \text{ cm}^{-1}$. The JT effect in the ${}^2E''$ state is very weak: $\alpha_e(\text{F-Ce-F}) = 119.5^\circ$, $E_{JT} = 2 \text{ cm}^{-1}$. The PJT coupling ($A_2'' + E''$) $\otimes e'$ results in strongly anharmonic adiabatic potential energy surface (APES) in the ${}^2A_2''$ ground state. The SO coupling enhances the anharmonic character of APESs due to both SO-quenching of JT distortions and the ${}^2A_2''$ state mixing in spin-coupled states. In all of the spin-orbit states the CeF_3 molecule is non-planar (C_{3v}) with the $C_{3v} \rightarrow D_{3h} \rightarrow C_{3v}$ inversion barrier height $h = 90\text{--}330 \text{ cm}^{-1}$.

The vibronic model Hamiltonian $(A_2'' + E' + E'' + A_1' + A_2') \otimes (a_1' + e' + e' + a_2')$ is constructed and parametrized for CeF_3 . The JT and PJT coupling constants are determined by a fitting of the calculated APESs. To describe the complicated vibronic coupling of the electronic states by the out-of-plane bending mode a_2'' , the relevant coupling constants are evaluated via the fitting of quasidiabatic MRCI potential energy surfaces generated by an approximate diabaticization procedure. To include SO coupling of the $A_2'' + E' + E'' + A_1' + A_2'$ electronic multiplet in the model Hamiltonian, the zeroth-order SO coupling constants are evaluated.

The eigenstates of the spin-vibronic Hamiltonian are calculated variationally and compared with the published infrared absorption spectrum of CeF_3 . The assignments of the observed spectral features are suggested.

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