Spin–orbit coupling and intersystem crossing (between $^4\Delta$ and $^6\Delta$ states) in iron monocyanide (FeCN)

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Studying and analysis of the interstellar medium (ISM) requires joint efforts from several fields: astronomy – observation with telescopes; astrophysics – physics laboratory experiments for obtaining plasma parameters (because nearly all of the ISM phases possess sufficient ionization for plasma behavior); and astrochemistry – experimental and theoretical analysis of molecules that exist in outer space.

We are particulary interested in one of these molecules, namely the radical FeCN. In 2011, FeCN was detected via radio telescope observation of the asymptotic giant branch star IRC+10216. It was the first Fe-bearing molecule that was detected in the interstellar medium. In this work we analyze the spin-orbit interaction in the low-lying states of this species. Our approach is quantum chemical, more precisely we intend to apply the multi-reference electronic structure methods.

Many low-lying states of FeCN have potential energy surfaces near the ground state surface, which give us a very complex electronic structure. In the first comprehensive theoretical investigation of low-lying electronic states of FeCN [1], the relative order of electronic states was proposed as follows: $^6\Delta$ (0 cm^{-1}), $^6\Pi$ (1800 cm^{-1}), $^4\Delta$ (2500 cm^{-1}), $^4\Pi$ (2900 cm^{-1}). The latest theoretical results of DeYonker [2] reported that a $^4\Delta$ ground state is lower than $^6\Delta$ state by only 306 cm^{-1}. By means of millimeter-wave rotational spectroscopy [3], and Fourier-transform microwave (FTMW) spectroscopy [4], the quartet was assigned as ground state of FeCN. The question that could be important is the transition between these states, i.e. is the expected rate of the intersystem crossing (quartet – sextet) significant. Useful information to answer this question can be obtained from the spin-orbit coupling matrix elements between states in question.

All electronic structure calculations have been performed using ORCA quantum chemistry software package [5]. First, we use the ORCA optimizer to locate the point of lowest energy of the crossing surfaces of $^4\Delta$ and $^6\Delta$ states (called the minimum energy crossing point, MECP). The level of theory for the optimization was the state averaged complete active space SCF with 13 electrons in 12 valence orbitals [SA-CASSCF (13,12)], with averaging two components of each degenerate state. Also, we use the scalar relativistic Douglas-Kroll-Hess (DKH) Hamiltonian and relativistically recontracted versions of the Karlsruhe basis set (ma-DKH-def2-QZVPP). Further, we calculate spin-orbit coupling matrix elements between $^4\Delta$ and $^6\Delta$ states at three different geometries: MECP geometry, the quartet state minimum and at the sextet state minimum geometry. The level of theory used is NEVPT2 (an internally contracted multireference perturbation theory), applied to SA-CASSCF wavefunctions with DKH and ma-DKH-def2-QZVPP basis set.

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