

Theoretical Determination of Charge-Transfer and Ligand Field Transition Energies for FeCl_4^- Using the EOM-CCSD Method

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The electronic structure of FeCl_4^- is an important model for ferric active sites, which exist in a large number of proteins and enzymes. FeCl_4^- has a *high-spin*, d^5 electronic configuration in its ground state and a geometric structure in which ligands are arranged around the iron center in (approximately) tetrahedral symmetry. As a model problem for ferric active sites in biological molecules, the theoretical determination of electronic excitation energies and oscillator strengths for FeCl_4^- is pertinent to understanding the role played by these active sites in various biological processes.

An *ab initio* determination of the spectrum of excitation energies for a transition-metal complex such as FeCl_4^- offers a demanding initial example for the energy-of-motion coupled cluster (EOM-CC) approach.^{1–4} Besides being an open shell, the molecule has 95 electrons, and even with the use of relativistically correct effective core potentials, the number of electrons that need to be correlated is 45. Other methods for determining excitations include a second-order perturbation theory based on a complete active space self-consistent field reference (CASPT2),^{5,6} and symmetry-adapted cluster–configuration interaction (SAC-CI),⁷ which have also been used for the ligand field spectra of transition-metal complexes.^{6,7}

EOM-CC is a recently developed, highly correlated method for the determination of electronic excitation energies.^{1,3,4} EOM-CCSD is conveniently single reference in concept, yet it is built upon a highly correlated coupled-cluster single and double excitation (CCSD) ground-state description, with the excited states being represented by all single and double excitations from the CCSD ground state. In this way, the theory introduces differential correlation effects. In prior applications to ketene, ethylene, norbornadiene, and chlorine peroxide, as well as several small molecules like N_2 , CO , O_3 , CH^+ , and Be , this method has been shown to yield accurate electronic transition energies ($\pm \sim 0.3$ eV) and oscillator strengths for excitations which are comparatively well described by single electron excitations.^{3,4} In this paper, we present the first EOM-CCSD results for a transition-metal

complex. We use the ACES II program system⁸ and a spherical basis set which includes an ECP description of the core electrons.⁹ The basis is listed in Table 1. The f function in the iron basis is added to correlate the iron d electrons since they are directly involved in the excitations of interest. The EOM-CCSD results require the determination of $\sim 700\,000$ single and double excitation coefficients.

The theoretical calculations are for the single molecule (gas phase), whereas the experiments are performed using a single crystal of $[\text{PPh}_4][\text{FeCl}_4]$. The experimental environment of the FeCl_4^- is reported to be “rigorous S_4 crystallographic symmetry, with effective D_{2d} molecular symmetry”.¹⁰ The D_{2d} distortion of the optimal gas-phase T_d geometry is small, with a compressed Cl–Fe–Cl angle of 114.6° .

We use 2.19 Å for the bond length, which is the average Fe–Cl distance from the X-ray structure,¹¹ and T_d symmetry for the charge-transfer excitations which occur within the sextet electronic manifold. The latter is supported by the small distortion from T_d in the crystal spectrum. We determine 0.03 eV as the energy change for the ground 6A_1 state to the experimental D_{2d} distorted geometry. The EOM-CCSD results for the first three excitation energies and relative intensities of the sextet charge-transfer transitions as well as the corresponding experimental results determined from Figure 12 in ref 10 are presented in Table 1. Recognizing that the experimental values are from a crystalline environment, the agreement with experiment for both excitation energies and intensities is good. The average excitation level (AEL)⁴ for all three transitions is close to 1.1, indicating that these transitions are well described by single electron excitations. An analysis of the ground- and excited-state wave functions indicate that all three transitions are charge-transfer in character. Each of the transitions yields a shift in electron density from the chlorine ligands to the iron center, in agreement with the conclusions drawn from the experimental photoelectron spectrum.¹²

We employ the experimental D_{2d} geometry in the calculation of the ligand field transition energies, which are presented in Table 2. This provides a symmetric SCF wave function for use in single reference CCSD(T) and EOM-CCSD calculations. We determine the spin-forbidden ${}^6A_1 \rightarrow {}^4A_2$ transition (${}^6A \rightarrow {}^4B$ in the D_2 subgroup of D_{2d} used in the calculations) using the difference of total energies obtained from two separate calculations on the respective states at both the CCSD and CCSD(T) levels of theory. Unlike EOM-CCSD, which permits obtaining all states of the same symmetry, as in the charge-transfer states, only a few states of different symmetry may be obtained with the single reference CC method.

The effect of the triple excitation estimate included in ROHF-CCSD(T)¹³ is important for the lowest energy; the CCSD energy is almost 0.5 eV away from the experimental value. We were able to determine (with effort because of the necessity of converging a single determinant reference) the energy of the lowest two 4B_1 and 4B_2 states (using the D_2 subgroup symmetry labels) at the CCSD and CCSD(T) levels of theory. While the triples estimate for the sextet-to-quartet transition is important, the

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(8) ACES II, an *ab initio* program system, authored by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett. The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor; the ABACUS integral derivative program of T. U. Helgaker, H. J. A. Jensen, P. Jørgensen, and P. R. Taylor; and the PROPS property integral package of P. R. Taylor. The ECP routines have been implemented in ACES II by C. Huber, University of Karlsruhe, Germany.

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Table 1. Excitation Energies (ΔE in eV) and Relative Intensities (I , Given as a Ratio of Oscillator Strengths for the Theoretical Results) for Optical Transitions from the 6A_1 State of FeCl_4^- (The basis set utilized effective core potentials^a with 6s5p3d1f on Fe and 3s3p on Cl.)

transition	EOM-CCSD		expt ^b	
	ΔE	I	ΔE	I
${}^6A_1 \rightarrow {}^6T_2$	3.50	1.00	3.41	1.00
${}^6A_1 \rightarrow {}^6T_2$	3.87	0.63	3.89	0.87
${}^6A_1 \rightarrow {}^6T_2$	4.29	0.45	4.55	0.48

^a Reference 9, with an f exponent of 2.0. ^b Reference 10.**Table 2.** Ligand Field Splitting Energies (ΔE in eV) for the Quartet Manifold of FeCl_4^-

transition D_2 symmetry ^a	EOM-CCSD	AEL	ΔCCSD	$\Delta\text{CCSD(T)}$	expt ^b
${}^6A \rightarrow {}^4B_1$			2.08	1.78	1.60
${}^4B_1 \rightarrow {}^4B_2$	0.43	1.09	0.21	0.19	0.17
${}^4B_1 \rightarrow {}^4B_1$	0.43	1.09	0.31	0.27	0.29
${}^4B_1 \rightarrow {}^4B_2$	0.95	1.09	0.69	0.65	0.39
${}^4B_1 \rightarrow {}^4A$	0.86	1.08			0.64

^a The first transition is from the 6A ground state to the lowest quartet state, 4B_1 . The other transitions represent energy differences with the 4B_1 state. All transitions are forbidden. The geometry is the experimental D_{2d} geometry, computations use the D_2 subgroup, and the associated state symmetry designations are given below. In D_{2d} , the transitions in order are ${}^6A_1 \rightarrow {}^4A_2$, ${}^4A_2 \rightarrow {}^4E$, ${}^4A_2 \rightarrow {}^4A_2$, ${}^4A_2 \rightarrow {}^4E$, and ${}^4A_2 \rightarrow {}^4A_1$, respectively. As used in ref 10, in T_d the transitions in order are ${}^6A_1 \rightarrow {}^4T_1(z) \rightarrow {}^4T_1(x,y)$, ${}^4T_1(z) \rightarrow {}^4T_2(z)$, ${}^4T_1(z) \rightarrow {}^4T_2(x,y)$, and ${}^4T_1(z) \rightarrow {}^4E$, respectively. ^b Reference 10.

energy level splitting within the quartet manifold seems to be insensitive to its inclusion.

We report three of the four possible D_2 symmetries. The B_3 symmetry block is degenerate with the B_2 symmetry block in the full D_{2d} symmetry (they are the two components of the E sym-

metry block). The A symmetry state is in good agreement with the experiment and demonstrates the value of EOM-CCSD, where ΔCC results are not possible (or very difficult to obtain). The second root in the 4B_2 symmetry block has a larger disagreement with the corresponding experimental value than the rest of the transition values (0.56 eV). The EOM-CCSD value, relative to the ΔCC value, however, is similar to that of the other quartet transitions, being ~ 0.2 eV higher. Contrary to the coupled-cluster results presented here, which involve no adjustable parameters, the $X\alpha$ results presented in ref 12 do not resolve the four transitions from the 6A ground state to the lowest two 4B_1 and 4B_2 states. Instead they report agreement to 0.14 eV with the average of the four experimental values.

In summary, EOM-CCSD yields very good results for the charge-transfer transitions from the 6A_1 ground state. Unlike EOM-CC, no single reference method is applicable for those states, as for most excited states. For the quartet manifold, where the ΔCC transition energies are available, they are in somewhat better agreement with experiment than are those obtained using EOM-CCSD. This potentially reflects the advantages of the exponential, $\exp(T_1 + T_2)\Phi_0$, description. The T_1T_2 products introduce disconnected triple excitations into the excited states, compared to the linear sum of all single and double excitations in EOM-CCSD. Both, of course, use a CC description for the ground state. The EOM-CC method has great potential as it applies to nearly all excited states. Including the effect of triple excitations into the excited states¹⁴ would extend the reliability of the method, particularly to two-electron transitions. These initial results for excitation energies in a transition-metal complex are promising and, due to the availability of EOM-CCSD in ACES II, point the way to many such improved applications.

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