Multireference perturbation study of \( \text{ClF}_4^+ \)

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The potential energy surface of \( \text{ClF}_4^+ \) has been investigated using a multiconfiguration SCF reference second-order quasidegenerate perturbation theory (MC-QDPT) method with a cc-pVTZ basis set. It is shown that the \( D_{4h} \) structure corresponds to a transition state, which connects two permutational isomers of the \( C_2v \) structure, and the \( C_{4v} \) structure also corresponds to a transition state for Berry pseudorotation, and connects two permutational isomers of the \( C_{2v} \) global minimum, as for the Hartree–Fock surface characterised in previous work.

I. Introduction

Interhalogen compounds have been much studied because they represent an unusual class of hypervalent stereochemically non-rigid molecules with interesting internal rearrangement mechanisms (Berry pseudorotation, turnstile rotation, Bar-tell mechanism, lever mechanism, etc.). For example, \( \text{ClF}_4^+ \) has a trigonal bipyramidal structure with one equatorial site vacant (\( C_2v \) symmetry), which is consistent with vibrational and \( ^19\text{F} \) NMR spectra as well as with VSEPR concepts. In such tetracoordinated molecules, Berry pseudorotation exchanges both axial with two equatorial ligands simultaneously, while the lever mechanism exchanges only one axial ligand with one equatorial ligand. The temperature dependence of the \( ^19\text{F} \) NMR spectra indicates that rapid fluorine ligand exchange in \( \text{ClF}_4^+ \) occurs in a solution of \( \text{ClF}_2\text{HF} \text{AsF}_5 \), although whether this is interior or intra-ligand exchange has not been elucidated.

In order to clarify the internal rearrangement mechanism, Minyaev and Wales previously investigated stationary points and the internal pseudorotation and inversion pathways on the potential energy surface (PES) of \( \text{ClF}_4^+ \), using spin-restricted Hartree–Fock (RHF) and second order Møller–Plesset perturbation theory (MP2), with basis sets of double-zeta plus polarization and \( ^19\text{F} \) NMR spectra as well as with VSEPR concepts. In such tetracoordinated molecules, Berry pseudorotation exchanges both axial with two equatorial ligands simultaneously, while the lever mechanism exchanges only one axial ligand with one equatorial ligand. The temperature dependence of the \( ^19\text{F} \) NMR spectra indicates that rapid fluorine ligand exchange in \( \text{ClF}_4^+ \) occurs in a solution of \( \text{ClF}_2\text{HF} \text{AsF}_5 \), although whether this is interior or intra-ligand exchange has not been elucidated.

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Very recently Mauksch and Schleyer have investigated the Berry and lever mechanisms in the topomerization of \( \text{SF}_4 \) and related tetracoordinated \( AX_4 \) species including \( \text{ClF}_4^+ \), using the hybrid DFT method B3LYP (Becke’s three parameter non-local hybrid exchange potential, using the hybrid DFT method B3LYP (Becke’s three parameter non-local hybrid exchange potential, using the local correlation functional of Lee, Yang, and Parr), and characterized the \( D_{4h} \) stationary point of \( \text{ClF}_4^+ \) as a second-order saddle point with two imaginary frequencies. Their result suggests that the transition state for the inversion has lower symmetry than \( D_{4h} \), with a lower activation energy. However, the B3LYP method employed in that study is based on a single electron configuration, and is not appropriate for such a multiconfigurational problem. In the present study we apply multiconfigurational and multireference electronic structure methods to investigate the PES of \( \text{ClF}_4^+ \) more accurately.

II. Computational details

We investigated three stationary points of \( \text{ClF}_4^+ \) with symmetries \( D_{4h} \), \( C_{4v} \), and \( C_{2v} \), as illustrated in Fig. 1. For the \( D_{4h} \) structure there is only one geometrical parameter, namely the bond length of Cl–F [\( r(\text{ClF}) \)]. Within this \( D_{4h} \) symmetry subspace, we calculated one-dimensional potential energy curves for the two lowest electronic states of \( ^3\text{A}_{1g} \) symmetry using the (equally-weighted) state-averaged complete active space multiconfigurational self-consistent field approach (SA-CASSCF) followed by multiconfiguration SCF reference second-order quasidegenerate perturbation theory (MC-QDPT). The lowest energy ground state \( D_{4h} \) geometry was obtained at the MC-QDPT level, and vibrational frequencies were evaluated through numerical differentiation of MC-QDPT energies. For the \( C_{4v} \) and \( C_{2v} \) structures the state-specific CASSCF method was applied to determine geometries and vibrational frequencies in the ground state. We employed a cc-pVTZ basis set in the Cartesian representa-
tion (6d, 10f) throughout. All calculations were carried out using GAMESS\textsuperscript{17} except for the evaluation of the analytical Hessian at the CASSCF level, for which we used GAUSSIAN 98.\textsuperscript{18}

For the $D_{4h}$ structure, the CASSCF active space consisted of all valence $p$ orbitals, \textit{i.e.}, Cl-3p and F-2p [24 electrons over 15 orbitals; denoted as (24/15)], resulting in 8212 (63700) configuration state functions of $A_g$ (A) symmetry in the $D_{2h}$ ($C_1$) point group. ($D_{4h}$ symmetry could not be used because of a restriction in the program.) The CASSCF active space was employed as the reference space in the MC-QDPT calculations. In the CASSCF geometry optimization and frequency calculations for the $C_n$, $C_{2n}$ structures, these active spaces were reduced to (8/7) and (10/8), respectively, based on the CI coefficients determined with the (24/15) active space.

### III. Results and discussion

As a preliminary survey, we first applied the RHF and MP2 methods to determine potential energy curves for the two lowest $^1A_{1g}$ states of $D_{4h} \text{ClF}_4^-$ as a function of $r(\text{ClF})$. At the RHF level, these two states both show a minimum around $r(\text{ClF}) = 1.6 \text{ Å}$, with an energy difference of 78 kcal mol$^{-1}$. The electronic configuration in the higher state is obtained by a double excitation from one high-lying occupied molecular orbital ($a_{2u}$) to one low-lying unoccupied molecular orbital ($a_{1g}$). Fig. 2 shows plots of these molecular orbitals generated by the Molden program.\textsuperscript{19} They both have antibonding character between Cl and F ($a_{1g}$ is in-plane; $a_{2u}$ is out-of-plane). We will refer to the configuration in the lower-lying state as config-I and the configuration in the higher state as config-II. At the MP2 level the config-II state is stabilized much more by electron correlation than the config-I state, especially in the region of longer Cl–F bond lengths, resulting in the interchange of the ground and excited states from the RHF results. The equilibrium bond distance of Cl–F in the config-II state changes significantly (∼ 2.00 Å), while, in the config-I state, it becomes slightly larger than the RHF value (∼ 1.65 Å). Note that the MP2 energy of the $D_{4h}$ minimum in the ground state was previously reported to be lower than that of the $C_{2v}$ minimum,\textsuperscript{5} which corresponds to the global minimum at the RHF level.

Moving to multiconfigurational approaches, we first performed state-averaged CASSCF (SA-CASSCF) calculations for the two lowest $^1A_{1g}$ states with equal weights, then carried out MC-QDPT calculations, to see the relation between these two electronic states. Fig. 3 shows potential energy curves for the two lowest $^1A_{1g}$ states with equal weights, then carried out MC-QDPT calculations. For the $D_{4h}$ stationary point, the harmonic frequency of the totally symmetric $a_{1g}$ mode was determined by fitting MC-QDPT energies with a step of 0.2 a 0 amu$^{-1/2}$. The resulting harmonic frequencies are $\nu_1 (a_{1g}) = 932 \text{ cm}^{-1}$; $\nu_2 (a_{2u}) = 618 \text{ cm}^{-1}$; $\nu_3 (b_1g) = 594 \text{ cm}^{-1}$; $\nu_4 (b_2g) = 447 \text{ cm}^{-1}$; $\nu_5 (b_1u) = 47 \text{ cm}^{-1}$; $\nu_6 (e_u) = 876 \text{ cm}^{-1}$; $\nu_7 (e_g) = 431 \text{ cm}^{-1}$. Hence, this stationary point is a true transition state\textsuperscript{20} (a saddle of Hessian index one), which connects two permutational isomers of the $C_{4v}$ structure via an $a_{2u}$ deformation.

Next we considered the $C_n$ and $C_{2n}$ stationary points of $\text{ClF}_4^-$ and $\text{ClF}_4$. First we carried out single point calculations for $C_n$, $C_{2n}$ structures by the CASSCF method using an active space of 24 electrons in 15 orbitals, (24/15). The orbitals that were doubly occupied in all configuration state functions with weights of more than 0.0025 were then excluded to give active

Fig. 3 Potential energy curves for the two lowest $^1A_{1g}$ states of $D_{4h} \text{ClF}_4^-$ calculated by the (a) SA-CASSCF and (b) MC-QDPT methods.
spaces of the form (8/7) and (10/8) for the \( C_{4v} \) and \( C_{2v} \) structures, respectively. Using these active spaces, geometrical parameters were determined at the CASSCF level: \( r(\text{CIF}) = 1.606 \text{ Å} \) and \( \theta(F_{1}\text{CIF}) = 144.8 \) degrees in the \( C_{4v} \) structure; \( r(\text{CIF}) = 1.565 \text{ Å} \), \( r(F_{2}\text{CIF}) = 1.610 \text{ Å} \), \( \theta(F_{1}\text{CIF}) = 116.8 \) degrees, and \( \theta(F_{2}\text{CIF}) = 165.3 \) degrees in the \( C_{2v} \) structure. The weights of the dominant configuration are 0.88 and 0.90 for the \( C_{4v} \) and \( C_{2v} \) structures, respectively. According to the analytical Hessian at the CASSCF level, the harmonic frequencies for the \( C_{4v} \) structure are \( v_1 (b_{2}) = 358 \text{ cm}^{-1} \); \( v_2 (a_{1}) = 643 \text{ cm}^{-1} \); \( v_3 (a_{1}) = 474 \text{ cm}^{-1} \); \( v_4 (b_{1}) = 542 \text{ cm}^{-1} \); \( v_5 (b_{2}) = 531 \text{ cm}^{-1} \); \( v_6 (e) = 715 \text{ cm}^{-1} \); \( v_7 (e) = 509 \text{ cm}^{-1} \). The harmonic frequencies for the \( C_{2v} \) structure are \( v_1 (a_{1}) = 702 \text{ cm}^{-1} \); \( v_2 (a_{1}) = 553 \text{ cm}^{-1} \); \( v_3 (a_{1}) = 505 \text{ cm}^{-1} \); \( v_4 (a_{1}) = 108 \text{ cm}^{-1} \); \( v_5 (b_{1}) = 785 \text{ cm}^{-1} \); \( v_6 (b_{1}) = 450 \text{ cm}^{-1} \); \( v_7 (b_{2}) = 735 \text{ cm}^{-1} \); \( v_8 (b_{2}) = 548 \text{ cm}^{-1} \); \( v_9 (a_{2}) = 525 \text{ cm}^{-1} \). Thus, the \( C_{4v} \) structure also corresponds to a transition state, which connects two permutational isomers of the \( C_{2v} \) minimum via a \( b_{2} \) deformation.

In summary, the \( D_{4h} \) structure is a transition state, which connects two permutational isomers of the \( C_{4v} \) structure, and the \( C_{4v} \) structure also corresponds to a transition state, which connects two permutational isomers of the \( C_{2v} \) global minimum, as for the RHF surface characterised in previous work. The relative energies of the respective stationary points are 48.1 kcal mol\(^{-1} \) (\( D_{4h} \)), 4.4 kcal mol\(^{-1} \) (\( C_{4v} \)), and 0 kcal mol\(^{-1} \) (\( C_{2v} \)) at the MC-QDPT level.

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References