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REGULAR ARTICLE

# Determination of molecular properties for moscovium halides (McF and McCl)

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## Abstract

Advanced relativistic quantum chemistry calculations were used for the first time to provide accurate determinations of fundamental molecular properties for two moscovium halides (McX, X = F and Cl). The recommended values presented here were obtained with the X2C-MMF-CCSD-T/RPF-4Z level of theory. Thus, we determined an equilibrium bond length ($r_e$) of 2.287 Å, an equilibrium dipole moment ($\mu_e$) of 6.59 D and a harmonic vibrational frequency ($\omega_e$) of 405 $\text{cm}^{-1}$ for McF. On the other hand, the results for McCl show $r_e$, $\mu_e$ and $\omega_e$ values equal to 2.728 Å, 7.46 D and 244 $\text{cm}^{-1}$, respectively. The same $\text{Mc}^+$–$\text{X}^-$ polarity is predicted in molecules of both halides. The equilibrium dissociation energies attained in X2C-MMF-(FS)CCSD/RPF-4Z calculations are 4.04 and 3.45 eV for McF and McCl, respectively. Therefore, the Mc–F and Mc–Cl bonds are predicted to be slightly stronger than Bi–F and Bi–Cl ones, respectively. Finally, the huge values obtained for dipole moments in the molecules studied strongly suggest that moscovium halides are predominantly ionic compounds.

**Keywords** Relativistic calculations · Moscovium · Spectroscopic data · Superheavy elements · Chemical properties

## 1 Introduction

In general, the experimental measurements of properties for superheavy elements (SHEs) are challenging because the whole process is expensive and there are inherent complications since these elements emit high-energy radiation and also exhibit short lifetimes [1, 2]. Moreover, it is well known that the electronic structure of SHEs is strongly affected by relativistic effects, which may provide sudden variations in atomic properties along columns that raise questions regarding their correct placement in the periodic table [3]. Hence, relativistic quantum chemistry is considered an advantageous tool for the determination of fundamental atomic and molecular properties in SHEs and their compounds [2, 4].

The SHE 115 was firstly synthesized in 2003 [5], being named as moscovium (Mc) according to the IUPAC recommendations from 2016 [6]. However, theoretical studies were used to predict some of its properties before the experimental discovery of this element and more recently as well [7–10]. Some of these previous investigations demonstrated, for example, that Mc is expected to present a monovalent state alternatively to the traditional trivalent state of lighter group 15 elements [7]. In this case, the compounds McH and $\text{McH}_3$ were already studied [8, 10].

The relativistic corrections in electronic structure studies can be split into two categories, scalar relativistic effects and spin–orbit coupling [11]. Actually, Dirac–Coulomb (DC) calculations done by means of the four-component formalism are used for an accurate description of all these relativistic corrections. However, some two-component Hamiltonians can provide similar results with lower demands for computational resources, such as the exact-two-component treatment with molecular mean field, X2C-MMF, which includes spin–orbit coupling as well as scalar relativistic effects [12].

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As occurs in nonrelativistic electronic structure studies, the selection of basis sets is also an important aspect in relativistic quantum chemistry. Nowadays, two different families of relativistic Gaussian basis sets are easily found, those from Dyall (dyall.v3z and dyall.v4z) [13, 14] and the RPF-4Z (relativistic prolapse-free basis sets of quadruple-zeta quality) from Teodoro et al. [15–17]. However, the RPF-4Z sets show some theoretical and practical advantages, being free of variational prolapse and requiring less computational resources when compared to quadruple-zeta basis sets from Dyall [15].

Therefore, we determined some fundamental molecular properties for two moscovium halides, McF and McCl, by means of advanced relativistic coupled-cluster calculations including iterative single and double excitations together, when possible, with a perturbative correction for triple substitutions (CCSD-T) [18].

## 2 Theoretical methods

All calculations were done with the DIRAC16 [19] package by means of a speed-of-light value of 137.0359998 a.u. The relativistic treatment was carried out by means of the exact-two-component molecular-mean-field (X2C-MMF) Hamiltonian [12] and the Gaussian nuclear model [20]. We performed CCSD-T calculations with three different relativistic basis sets: dyall.v3z [13, 14], dyall.v4z [13, 14] and RPF-4Z [15]. All the basis sets were used in their uncontract form, and in addition, the small components functions (S) were obtained by means of standard kinetic balance conditions. Furthermore, the (SS|SS) integrals were substituted by an approximated treatment to reduce the computational demand [21]. The active space is composed by 22 correlated electrons for McF and McCl and virtual spinors up to 20.0 a.u., with minimum gap of 1.0 a.u., corresponding to the valence and some of the sub-valence electrons of moscovium (6*d*, 7*s* and 7*p*), fluorine (2*s* and 2*p*) and chorine (3*s* and 3*p*).

The potential energy curves (PECs) of these two molecules (McF and McCl) were studied by single-point calculations in seven points distributed around a central value of bond length (near the equilibrium geometry) with a variation of 0.01 Å between them. These energy results are displayed in Tables S1 and S2 (Supplementary Material). In the sequence, we used the TWOFIT utility program, as distributed within DIRAC16, for the determination of spectroscopic constants for the two molecules. The default masses were considered for F, Cl and Mc. The PECs were fitted by means of a fifth-order polynomial.

In addition, the dipole moment was determined by the analytical result from the Dirac–Hartree–Fock (DHF) treatment complemented by the electron correlation contribution ($\Delta\mu_{\text{corr}}$) obtained from a finite-difference technique in two-point form, that is,

$$\Delta\mu_{\text{corr}} = -\left(\frac{\partial E(\lambda)}{\partial\lambda}\right)_0 \approx -\left(\frac{E(+\lambda)-E(-\lambda)}{2\lambda}\right), \quad (1)$$

where $E$ is the correlation energy and the perturbation, $\lambda$, was taken as $1.0\times10^{-6}$ a.u. The theoretical equilibrium bond lengths were used in these calculations.

Finally, the dissociation energy was determined with X2C-MMF-CCSD energies for McF and McCl along with X2C-MMF results from additional Fock-space-coupled-cluster (FSCC) calculations by using closed shell systems ($\text{Mc}^+$, $\text{F}^-$ and $\text{Cl}^-$) as reference to obtain the required electron affinities and ionization potentials. The active space considered 14 electrons for $\text{Mc}^+$ and 8 electrons for $\text{F}^-$ and $\text{Cl}^-$, together with virtual spinors up to 20.0 a.u., again with a minimum gap of 1.0 a.u.

## 3 Results and discussion

Table 1 shows the equilibrium ground-state data obtained in this study for the McF molecule by X2C-MMF-CCSD-T calculations with different relativistic basis sets. We determined the equilibrium bond length ($r_e$), the harmonic vibrational frequency ($\omega_e$), the anharmonicity constant ($\omega_e\chi_e$), the equilibrium dissociation energy ($D_e$) and the dipole moment at $r_e$ ($\mu_e$). As mentioned, the $D_e$ values are obtained at the X2C-MMF-CCSD theory level once Fock-space calculations are required to achieve results for open-shell species and the energy results used in this determination are collected in Table S3 (Supplementary Material).

One can see that the basis sets with quadruple-zeta quality, RPF-4Z and dyall.v4z, provide quite similar results in these determinations. However, when compared to the values from these larger basis sets, the basis set of triple-zeta quality (dyall.v3z) results in larger deviations for $r_e$ ($\geq 0.012$ Å), $\omega_e$ ($\geq 6.5$ cm$^{-1}$), $D_e$ ($\geq 0.18$ eV) and $\mu_e$ ($\geq 0.07$ D). Our recommended values are obtained with the RPF-4Z basis set, which furnishes 2.2872 Å, 405.5 cm$^{-1}$, 2.20 cm$^{-1}$ and

**Table 1** Equilibrium ground-state data for McF as calculated at the X2C-MMF-CCSD-T level with three different relativistic basis sets

| Basis set | $r_e$ (Å) | $\omega_e$ (cm$^{-1}$) | $\omega_e\chi_e$ (cm$^{-1}$) | $D_e$ (eV)[a] | $\mu_e$ (D)[b] |
|---|---|---|---|---|---|
| dyall.v3z | 2.3021 | 397.2 | 2.32 | 3.85 | 6.70 |
| dyall.v4z | 2.2898 | 403.7 | 2.03 | 4.05 | 6.63 |
| RPF-4Z | 2.2872 | 405.5 | 2.20 | 4.04 | 6.59 |

[a] These X2C-MMF calculations were done with the Fock-space (FS) CCSD approach

[b] The polarity of this molecule is $\text{Mc}^+$–$\text{F}^-$

4.04 eV, respectively, for $r_e$, $\omega_e$, $\omega_e\chi_e$ and $D_e$. The $r_e$ value obtained here is in excellent agreement with the sum of covalent radii provided by Pyykkö and Atsumi for Mc and F [22], 2.26 Å. The dipole moment calculated with the RPF-4Z basis set was 6.59 D, indicating a $Mc^+–F^-$ polarity for this molecule.

The experimental data of $r_e$, $\omega_e$ and $D_e$ for the previous fluoride of Group 15, BiF, are 2.0516 Å, 513 $cm^{-1}$ and 3.79–3.9 eV, respectively [23, 24]. Thus, the $D_e$ values calculated here for McF are larger by 0.14–0.25 eV. Hence, these results indicate that the Mc–F bond is slightly stronger than the Bi–F one. On the other hand, the force constants that can be estimated from the $\omega_e$ values suggest that the Bi–F is more rigid than the Mc–F bond.

Next, Table 2 contains the $r_e$, $\omega_e$, $\omega_e\chi_e$, $D_e$ and $\mu_e$ values found for the McCl molecule. Again, the dyall.v3z basis set provides longer $r_e$, smaller $\omega_e$ and larger $\mu_e$ than those from the quadruple-zeta basis sets. The RPF-4Z basis set shows values for $r_e$, $\omega_e$, $\omega_e\chi_e$ and $D_e$ in McCl equal to 2.7284 Å, 243.8 $cm^{-1}$, 1.03 $cm^{-1}$ and 3.45 eV, respectively, and the dipole moment obtained with this basis set, 7.46 D, points to a similar polarity as that one seen for McF, $Mc^+–Cl^-$. The sum of covalent radii for Mc and Cl [22], 2.61 Å, results in a slightly smaller bond length than the one seen in our results.

The experimental values of $r_e$, $\omega_e$ and $D_e$ for BiCl are 2.4716 Å, 308 $cm^{-1}$ and 3.15 eV, respectively [23, 24]. Therefore, the $D_e$ increment as one moves from BiCl to McCl is 0.30 eV. As also occurred for the fluorides, the Mc–Cl bond is predicted to be slightly stronger and less rigid than the Bi–Cl one.

The moscovium ionization energies attained from X2C-MMF-FSCCSD calculations with dyall.v3z, dyall.v4z and RPF-4Z basis sets are 5.41, 5.49 and 5.48 eV, respectively, as can be seen from data in Table S3. These values are in excellent agreement with four-component CCSD(T) calculations found in the literature including Breit and quantum electrodynamics (QED) corrections, 5.57 eV (Breit and QED corrections together correspond to only 0.01 eV, and triple excitations increase the value by only 0.07 eV) [25].

DHF and electron correlation contributions to the dipole moments of McF and McCl are displayed in Table S4 (Supplementary Material). As one can see, the DHF contribution predominates, while the electron correlation decreases the dipole moment magnitude. The dyall.v3z basis set slightly overestimates both contributions as compared to results from quadruple-zeta quality basis sets (dyall.v4z and RPF-4Z). Finally, the huge dipole moments obtained in this work along with the small ionization potential of moscovium strongly suggest that McF and McCl are mostly ionic compounds, although a highly polarizable $7p_{1/2}$ lone electron pair is expected to be present at the moscovium end. This behavior could be anticipated considering the long-known huge effects of spin–orbit coupling over the $7p_{1/2}$ and $7p_{3/2}$ spinor energies of moscovium [26]. Therefore, the ionic radius of $Mc^{+1}$ can be estimated from our recommended $r_e$ data for McF and McCl along with the ionic radii provided by Pyykkö and Atsumi [22] for $F^-$ and $Cl^-$, resulting in 1.09–1.14 Å.

**Table 2** Equilibrium ground-state data for McCl as calculated at the X2C-MMF-CCSD-T level with three different relativistic basis sets

| Basis set | $r_e$ (Å) | $\omega_e$ ($cm^{-1}$) | $\omega_e\chi_e$ ($cm^{-1}$) | $D_e$ (eV)[a] | $\mu_e$ (D)[b] |
|---|---|---|---|---|---|
| dyall.v3z | 2.7497 | 239.8 | 0.70 | 3.64 | 7.60 |
| dyall.v4z | 2.7373 | 241.1 | 1.07 | 3.48 | 7.58 |
| RPF-4Z | 2.7284 | 243.8 | 1.03 | 3.45 | 7.46 |

[a] These X2C-MMF calculations were done with the Fock-space (FS) CCSD approach

[b] The polarity of this molecule is $Mc^+–Cl^-$

## 4 Conclusions

In conclusion, we used advanced relativistic quantum chemistry methods to report for the first time some molecular properties of moscovium halides, McF and McCl. The recommended values obtained for bond length, vibrational frequency, dipole moment and dissociation energy of McF are 2.287 Å, 405 $cm^{-1}$, 6.59 D and 4.04 eV, respectively. Accordingly, the respective results for McCl are 2.728 Å, 244 $cm^{-1}$, 7.46 D and 3.45 eV. The results obtained here point to predominant ionic character in the bonds of these moscovium halides, suggesting an ionic radius of 1.09–1.14 Å for $Mc^{+1}$.

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**Availability of data and material** All data generated or analyzed during this study are included in this published article (and its supplementary information files).

## Compliance with ethical standards

**Conflicts of interest** The authors declare that they have no conflict of interest.

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