Vibrational Frequencies, Structures, and Energetics of the Highly Challenging Alkali Metal Trifluorides MF$_3$ (M = Li, Na, K, Rb, and Cs)

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Physical Chemistry Chemical Physics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>CP-ART-05-2018-003434.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>29-Jun-2018</td>
</tr>
</tbody>
</table>
| Complete List of Authors: | Sun, Zhi; University of Georgia, Chemistry  
Schaefer, Henry; University of Georgia, Computational Chemistry |
Vibrational Frequencies, Structures, and Energetics of the Highly Challenging Alkali Metal Trifluorides

$\text{MF}_3$ ($\text{M} = \text{Li, Na, K, Rb, and Cs}$)

Zhi Sun and Henry F. Schaefer III*

*Center for Computational Quantum Chemistry, University of Georgia

*E-mail: ccq@uga.edu
Abstract

Many experimental studies have been reported on the alkali metal trifluorides MF$_3$ (M = Li, Na, K, Rb, and Cs), and several controversies remain. In the present research, we systematically study the MF$_3$ systems using both coupled-cluster and multireference methods. New predictions and explanations are provided for some known experimental and theoretical challenges, including identification of the true MF$_3$ minima and global minima, the unclear existence of light alkali metal trifluorides MF$_3$ (M = Li and Na), and assignment of the F-F-F symmetric stretch frequencies for the heavier alkali metal trifluorides MF$_3$ (M = K, Rb, and Cs). With several new structures located, we predict a preference of $C_s$ minima for MF$_3$ (M = Li and Na) and $C_{2v}$ minima for MF$_3$ (M = K, Rb, and Cs). For the species where multiple minima were located, near degeneracies of those minima can be found in most cases. The endothermicities (~3 - 4 kcal/mol) for the favored MF$_3$ → MF + F$_2$ fragmentations suggest that MF$_3$ (M = Li and Na) are weakly bonded complexes. The existence of those species at low temperatures cannot be ruled out, and vibrational frequencies are reported to guide future experiments. Most importantly, significant differences between the coupled-cluster and multireference results were found in predicting the F-F-F symmetric stretch frequencies ($\nu_s$) of the $C_{2v}$ MF$_3$ (M = K, Rb, and Cs) structures, although both methods show good performance in predicting most structures and antisymmetric stretch frequencies ($\nu_{as}$). The coupled-cluster [CCSD(T), CCSDT, and CCSDT(Q)] results agree with the recent experimental assignment of Redeker, Beckers, and Riedel [389 cm$^{-1}$, RSC Adv. 2015, 5, 106568] to the $\nu_s$ fundamental of CsF$_3$. In contrast, the multireference (CASPT2, CASPT3, and MRCISD+Q) results support the original experimental assignment of Ault and Andrews [461 cm$^{-1}$, J. Am. Chem. Soc. 1976, 98, 1591; Inorg. Chem. 1977, 16, 2024]. The F-F-F symmetric stretch frequencies for the MF$_3$ molecules (M = K, Rb, and Cs) continue to provide a great challenge to theory and experiment.
Introduction

The trifluoride anion $\text{F}_3^-$ is a highly challenging system for theoretical studies. Single-reference methods including DFT, MP$n$ ($n = 2, 3, \text{ or } 4$), configuration interaction (CI), and coupled-cluster (CC) produce largely inconsistent results for the structure, binding energy, and vibrational frequencies of $\text{F}_3^-$. Only the CI and CC methods including triple excitations [CCSD(T) and QCISD(T)] exhibit some reliability in achieving agreement with the experiments. Artificial symmetry-breaking issues ($D_{\infty h} \rightarrow C_{\infty v}$) appear in multireference treatments (MCSCF, for instance) with certain active spaces [(3o,4e) and (9o,14e)]. Theoretical results are also sensitive to the selection of active space, basis sets, and dynamic correlation.

The challenges associated with $\text{F}_3^-$ stem from its special bonding character. In addition to the two main Lewis structure contributors (Types I and II in Figure 1), another three-electron bonding type (Type III)

\[
\begin{array}{cccccc}
\text{F} & : & \text{F} & \text{F}^- & \text{F}^- & \text{F} : \text{F} & \text{F}^+ & \text{F}^- & \text{F}^+
\end{array}
\]

(I) \hspace{1cm} (II) \hspace{1cm} (III)

Figure 1. Valence-bond structures most often proposed for $\text{F}_3^-$. 

\[3\]
contributes significantly to the $F_3^-$ electronic structure, according to the 2004 valence bond (VB) study of Braïda and Hiberty.\textsuperscript{7} This special bonding character provides an explanation for its multireference and symmetry-breaking challenges in the theoretical studies mentioned above, as well as the peculiar preference of its energetically unfavorable dissociation channel into $F_2^- + F^\cdot$ at high collision energies, instead of $F_2 + F^-$.\textsuperscript{8}

Significant challenges remain for theoretical studies of the interactions between $F_3^-$ and the alkali metal cations ($M^+$, $M = Li, Na, K, Rb, \text{ and } Cs$). One major difficulty is to identify the true minima of the $MF_3$ species. Specifically, inconsistent results were reported in previous attempts to determine which structure [asymmetric ($C_s$) or symmetric ($C_{2v}$) T-shape] in Figure 2 is the true minimum. The existing theoretical results exhibit strong method-dependence.\textsuperscript{9-12} This is very different from the $MX_3$ case when the halide $X$ is chlorine, bromine, or iodine. The $MX_3$ structures of the higher halides consistently favor the asymmetric ($C_s$) structure to be minimum, as suggested by the experiments of Ault and Andrews\textsuperscript{13} and a recent theoretical study.\textsuperscript{14}
Figure 2. Two isomers of MF\textsubscript{3} (M = Li, Na, K, Rb, and Cs) reported in the literature.

An early systematic study by Tozer and Sosa\textsuperscript{9} found that Hartree-Fock, MP2, QCISD, BLYP, and B3LYP give inconsistent results in their predictions of the MF\textsubscript{3} structures. Only the B3LYP functional reasonably predicts the metal-dependent minima (\textit{C}_\text{s} NaF\textsubscript{3}; \textit{C}_\text{2v} KF\textsubscript{3}, RbF\textsubscript{3}, and CsF\textsubscript{3}, see Figure 2) align with the results inferred from the IR/Raman spectra by Ault and Andrews.\textsuperscript{15,16} The \textit{C}_\text{2v} minima for KF\textsubscript{3} and CsF\textsubscript{3} were recently (2015) predicted at the CCSD(T)/def2-QZVPP level of theory by Andrews, Riedel and coworkers.\textsuperscript{12} The \textit{C}_\text{s} symmetry KF\textsubscript{3} and CsF\textsubscript{3} structures were not reported there because the \textit{C}_\text{s} structures (see Figure 2) were selected as the initial geometries for optimization which lead to the \textit{C}_\text{2v} minima. In contrast, in the same year (2015), Hoffmann and coworkers located the \textit{C}_\text{s} CsF\textsubscript{3} structure as a minimum with the PBE0/TZVP/ZORA method, whereas the \textit{C}_\text{2v} CsF\textsubscript{3} structure was found to be a transition state connecting the two equivalent \textit{C}_\text{s} CsF\textsubscript{3} structures with a small barrier of \textasciitilde1 kcal/mol.\textsuperscript{17} Another paper, published in 2015 by Getmanskii and coworkers, mainly focuses on MF\textsubscript{3} with light alkali
metals (M = Li, Na, and K).\textsuperscript{10} Apparently Getmanskii disagrees with the B3LYP results from Tozer and Sosa,\textsuperscript{9} because both $C_6$ and $C_{2v}$ NaF$_3$ isomers were predicted by Getmanskii and coworkers to be minima at the CCSD(T)/6-311+G(3df) level of theory, with the $C_{2v}$ NaF$_3$ structure lying slightly higher (~0.2 kcal/mol, ZPVE corrected).

Another challenge for theoretical studies is to examine the experimental vibrational spectra of the MF$_3$ systems. The four papers concerning the MF$_3$ vibrational frequencies in inert matrices by the groups of Andrews, Beckers, Riedel, and coworkers are particularly important.\textsuperscript{11, 12, 15, 16} According to the early experiments by Andrews and coworkers,\textsuperscript{15, 16} only large alkali metals cations (K$^+$, Rb$^+$, and Cs$^+$) can effectively form stable M$^+$F$_3^-\text{“ion pairs”}$ via the reaction MF + F$_2$. Vibrational frequency analyses exhibit two mutually exclusive IR and Raman bands which were proposed to be the antisymmetric and symmetric stretches of the F$_3^-$ moiety in MF$_3$, respectively. These vibrational frequencies are remarkably insensitive (different by ~1 cm$^{-1}$) to the metal identity (K, Rb, and Cs), indicating nearly pure fluorine vibrations not involving the metal very much. The structures of MF$_3$ (M = K, Rb, and Cs) were therefore proposed to be “T-shaped” with nearly linear and centrosymmetric ($D_{\infty h}$) F$_3^-$ units centered over the M$^+$ cation (see $C_{2v}$ structure in Figure 2).
For the vibrational frequencies, the IR bands (~550 cm\(^{-1}\) in argon,\(^{11, 15, 16}\) krypton,\(^{11}\) and nitrogen,\(^{11}\) or ~561 cm\(^{-1}\) in neon,\(^{11}\) metal-insensitive) have been assigned to the antisymmetric stretch (\(\nu_{as}\)) of the F\(_3^-\) unit in MF\(_3\) (M = K, Rb, and Cs), from the experiments of Andrews, Riedel, and coworkers.\(^{11, 12, 15, 16}\) This assignment has been recently supported by the computations of Andrews, Beckers, and coworkers using the CCSD(T) method (def2-TZVPP: 552 cm\(^{-1}\); def2-QZVPP: 568 cm\(^{-1}\), with anharmonic correction).\(^{12}\) However, the symmetric stretch frequency (\(\nu_s\)) of F\(_3^-\) in CsF\(_3\) is somewhat puzzling. A large deviation [theoretical: 388 cm\(^{-1}\) at the CCSD(T)/def2-QZVPP level of theory with anharmonic correction;\(^{12}\) experimental: 461 cm\(^{-1}\) in argon\(^{15, 16}\)] was found. In the early experiments of Andrews and coworkers,\(^{15, 16}\) two Raman bands (389 and 461 cm\(^{-1}\)) were reported. Upon diffusion (15 K \(\rightarrow\) 40 K \(\rightarrow\) 15 K), the 389 cm\(^{-1}\) Raman band decreased in intensity markedly, while the 461 cm\(^{-1}\) band remains intense. The former was then assigned to a short-lived unstable species, while the latter was connected to the 550 cm\(^{-1}\) IR band which also survives the diffusion procedure. As a result, the 461 and 550 cm\(^{-1}\) bands were assigned together to the symmetric and antisymmetric stretches of the F\(_3^-\) moiety in CsF\(_3\), respectively.

However, a 2015 paper by Riedel and coworkers\(^{11}\) provided a different interpretation and
suggested that the 389 cm\(^{-1}\) band in Andrews’s experiment\(^{15, 16}\) should be assigned to the symmetric stretch \(\nu_s\). Therein Riedel’s logic is that, except for the 550 cm\(^{-1}\) \(\nu_{as}\) band, a new IR band was located at ~920 cm\(^{-1}\) (argon: 923 cm\(^{-1}\); krypton: 919 cm\(^{-1}\)) and assigned to a possible combination band of \(\nu_{as}\) and \(\nu_s\) (\(\nu_{as} + \nu_s = 550 + 389 = 939\) cm\(^{-1}\)) in the CsF\(_3\) IR spectra. This new combination band vanished simultaneously with the 550 cm\(^{-1}\) \(\nu_{as}\) band upon irradiation (\(\lambda = 266\) nm), suggesting the two might belong to the same species. If this is true, the previously computed \(\nu_s\) at the 388 cm\(^{-1}\) at the CCSD(T)/def2-QZVPP level of theory\(^{12}\) agrees well with these experiments.\(^{11, 15, 16}\) However, the sustained and relatively intense 461 cm\(^{-1}\) Raman band\(^{15, 16}\) becomes puzzling if the 389 cm\(^{-1}\) is the final answer for the fundamental \(\nu_s\).

Last but not least, previous experiments suggest that the \(\text{M}^+\text{F}_3^-\) “ion pair” with the light alkali metals (Li and Na) cannot be effectively produced through the \(\text{MF} + \text{F}_2\) reaction.\(^{11, 12, 15, 16}\) However, the 2015 theoretical paper by Getmanskii and coworkers located both the \(C_s\) and \(C_{2v}\) minima (see Figure 2) for LiF\(_3\) and NaF\(_3\) at the CCSD(T)/6-311+G(3df) level of theory.\(^{10}\) The IR studies of the \(\text{MF} + \text{F}_2\) experiments clearly do not support the formation of LiF\(_3\) and NaF\(_3\) in \(C_{2v}\) symmetry, under the stated experimental conditions.\(^{11, 16}\) However, consistent with the B3LYP results by Tozer and Sosa,\(^9\) the CCSD(T)/6-311+G(3df) results suggest possible \(C_s\) minima. This
might be theoretical evidence for the Na$^+$F$^-$···F$_2$ complex proposed by Ault and Andrews.$^{16}$

In light of the challenges mentioned above, new theoretical research with rigorous computations are called for. The present study systematically investigates the MF$_3$ (M = Li, Na, K, Rb, and Cs) molecular systems and makes comparison with previous theoretical and experimental research to help characterize those species.

**Theoretical Methods**

Our initial coupled-cluster$^{18, 19}$ [CCSD(T), with restricted (RHF) and unrestricted (UHF) Hartree-Fock references for involved closed-shell and open-shell species, respectively] computations were performed using CFOUR 2.0,$^{20, 21}$ with the set of weighted core-valence basis sets noted below:

Li, Na: cc-pwCVTZ$^{22}$

K, Rb, Cs: cc-pwCVTZ-PP$^{22}$

F: aug-cc-pwCVTZ$^{23}$

All electrons are correlated in our CCSD(T) computations except when the Köln/Stuttgart effective core potentials (ECPs, K: ECP10MDF; Rb: ECP28MDF; Cs: ECP46MDF)$^{24}$ are used
to describe the inner cores of K \((1s^22s^22p^6)\), Rb \((1s^22s^22p^63s^23p^63d^{10})\), and Cs \((1s^22s^22p^63s^23p^64s^23d^{10}4p^64d^{10})\) elements. To make this discussion succinct, we will refer to the coupled-cluster method with the mixture of these basis sets simply as CCSD(T)/AWCVTZ. For the CCSD(T) computations, stringent criteria were set for the SCF densities \((10^{-10})\), CC amplitudes \((10^{-9})\), and RMS forces \((10^{-8} \text{ Hartree/Bohr})\). The anharmonic frequencies are obtained using second-order vibrational perturbation theory (VPT2).\(^{25}\)

As this investigation unfolded, far more sophisticated coupled cluster methods were adopted. Specifically, structures and vibrational frequencies were predicted with the full triples (CCSDT) and perturbative quadruples [CCSDT(Q)] methods.

Multireference (MR) computations were performed using Molpro 2010.1,\(^{26}\) with the CCSD(T)/AWCVTZ-optimized geometries as starting points. A relatively large \((16e,10o)\) active space (including F: 2p, Li: 2s, Na: 3s, K: 4s, Rb: 5s, and Cs: 6s) was first selected for the complete active space self-consistent field (CASSCF) single-point computations. Only the species with leading configuration lower than 90% (all \(C_{2v}\) structures, see supporting information, SI) were further treated with multireference configuration interaction method\(^{27, 28}\) with the Davidson correction,\(^{29}\) abbreviated as MRCISD+Q. Only the orbitals with occupation
number (from CASSCF) in the range of 0.02-1.98 were selected to construct a new active space for the MRCISD+Q optimization and frequency computations. Such an orbital selection strategy generates a consistent active space (4e,3o) and orbital set (one σ bonding, one nonbonding, and one σ* antibonding, Figure 3) for all five $C_2v$ structures for MF$_3$ (M = Li, Na, K, Rb, and Cs).

The MRCISD+Q(4e,3o) computations were performed following the CASSCF(4e,3o) computations. For all MR computations, the SCF energies and densities were both converged to $10^{-10}$, and the RMS forces were converged to $10^{-6}$ Hartree/Bohr. The valence basis sets for the MR computations are listed below.

- Li, Na: cc-pVTZ$^{30}$
- K, Rb, Cs: cc-pVTZ-PP$^{22}$
- F: aug-cc-pVTZ$^{31}$

We will refer to this multireference method with these mixed basis sets as MRCISD+Q(4e,3o)/AVTZ for simplicity. For comparison purposes, additional MR computations were performed using second-order multireference perturbation theory (CASPT2)$^{32, 33}$ based on the same active space used for the MRCISD+Q computations, and abbreviated as CASPT2(4e,3o)/AVTZ. The CASPT2 results generally align with the
MRCISD+Q results and therefore are only provided in the SI. Moreover, additional coupled-cluster [CCSDT and CCSDT(Q)] and third-order multireference perturbation theory (CASPT3) optimization and frequency were computed for CsF₃, which will be discussed later.

**Figure 3.** Orbitals (illustrated for LiF₃) included in the MRCISD+Q(4e,3o)/AVTZ computations for C₂ᵥ MF₃ (M = Li, Na, K, Rb, and Cs) with natural orbital occupation numbers (in brackets) obtained at the CASSCF(16e,10o)/AVTZ level of theory.

## Results and Discussion

### A. Performance of the Selected Theoretical Methods

The accuracy of the selected coupled-cluster method [CCSD(T)/AWCVTZ] will be assessed first. Relevant diatomic species MF (M = Li, Na, K, Rb, and Cs) and F₂ are chosen as a test set because the experimental information on the tetra-atomic MF₃ species is limited, especially for their structures. Gas phase experimental equilibrium bond distances and harmonic vibrational frequencies are obtained from the compilation of Huber and Herzberg. The benchmark results...
are listed in Table 1.

For the equilibrium bond lengths, mean absolute errors (MAE) and mean absolute percent errors (MAPE) were computed to be 0.012 Å and 0.6%, respectively. Small positive deviations from the experimental distances can be found for each species, with an increasing trend from LiF to CsF (0.3% to 1.1%). The deviation for F₂ is small, 0.005 Å and 0.4%. For the harmonic vibrational frequencies, the MAPE was computed to be 1.0%. In contrast to the bond lengths, negative deviations from the experimental harmonic vibrational frequencies can be noticed for all diatomics MF, with an increasing trend from LiF to CsF (0.5% to 2.3%). Again, the deviation for F₂ is small, 1 cm⁻¹ and 0.1%.

**Table 1.** Benchmark of the CCSD(T)/AWCVTZ equilibrium bond lengths (in Å) and harmonic vibrational frequencies (in cm⁻¹) of MF and F₂ (M = Li, Na, K, Rb, and Cs) molecules, against experimental values compiled by Huber and Herzberg (Ref. 34).

<table>
<thead>
<tr>
<th>Species</th>
<th>Computed</th>
<th>Experiment</th>
<th>Deviation</th>
<th>Percent Error</th>
<th>Computed</th>
<th>Experiment</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1.569</td>
<td>1.564</td>
<td>0.005</td>
<td>0.3%</td>
<td>905</td>
<td>910</td>
<td>0.5%</td>
</tr>
<tr>
<td>NaF</td>
<td>1.934</td>
<td>1.926</td>
<td>0.008</td>
<td>0.4%</td>
<td>531</td>
<td>536</td>
<td>0.9%</td>
</tr>
<tr>
<td>KF</td>
<td>2.183</td>
<td>2.172</td>
<td>0.011</td>
<td>0.5%</td>
<td>424</td>
<td>428</td>
<td>0.9%</td>
</tr>
<tr>
<td>RbF</td>
<td>2.286</td>
<td>2.270</td>
<td>0.016</td>
<td>0.7%</td>
<td>372</td>
<td>376</td>
<td>1.1%</td>
</tr>
<tr>
<td>CsF</td>
<td>2.371</td>
<td>2.345</td>
<td>0.026</td>
<td>1.1%</td>
<td>345</td>
<td>353</td>
<td>2.3%</td>
</tr>
<tr>
<td>F₂</td>
<td>1.417</td>
<td>1.412</td>
<td>0.005</td>
<td>0.4%</td>
<td>918</td>
<td>917</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

Mean: 0.012 0.6%  Mean: 1.0%
The dissociation energies ($D_0$) of the two $F_3^-$ dissociation channels are reported in Table 2, with the experimental values obtained from the Wenthold collision-induced dissociation experiments for comparison. The $D_0$ values for the $F_3^- \rightarrow F_2 + F^-$ and $F_3^- \rightarrow F + F_2^-$ dissociation channels are predicted to be 22.7 and 31.3 kcal/mol, respectively. These values deviate from experiment by ~1 kcal/mol.

Table 2. Endothermicities ($D_0$) of two $F_3^-$ dissociation channels at the CCSD(T)/AWCVTZ level of theory.

<table>
<thead>
<tr>
<th></th>
<th>Theory (present work)</th>
<th>Experiment (ref. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0 (F_3^- \rightarrow F_2 + F^-)$</td>
<td>22.7 kcal/mol</td>
<td>1.02 ± 0.11 eV (~23.5 kcal/mol)</td>
</tr>
<tr>
<td>$D_0 (F_3^- \rightarrow F + F_2^-)$</td>
<td>31.3 kcal/mol</td>
<td>1.30 ± 0.13 eV (~30.0 kcal/mol)</td>
</tr>
</tbody>
</table>

The initially chosen coupled-cluster method [CCSD(T)/AWCVTZ] predicts reliable structures, harmonic frequencies, and endothermicities for the selected test set. It is then expected to achieve satisfactory accuracy for the MF$_3$ systems and reasonably assess previous theoretical and experimental research. For those structures with strong multireference issues, MR methods (MRCISD+Q, CASPT2, CASPT3) will be applied and compared with the CCSD(T)
B. Light Alkali Metal Trifluorides: LiF$_3$ and NaF$_3$

The results for light alkali metal trifluorides (LiF$_3$ and NaF$_3$) at the CCSD(T)/AWCVTZ and MRCISD+Q(4e,3o)/AVTZ levels of theory are shown in Figures 4. As discussed in the Introduction, one major challenge for previous theoretical studies of MF$_3$ is to determine which structure ($C_s$ or $C_{2v}$) in Figure 2 is the true minimum (or global minimum). This will be the focus of the following discussion.

As shown in Figure 4, $C_s$ structures are found to be minima for both LiF$_3$ and NaF$_3$, while the $C_{2v}$ structures correspond to transition states connecting two equivalent $C_s$ structures. Interestingly, we located two different $C_s$ NaF$_3$ minima (loose- and tight-type). Like the case of $C_s$ LiF$_3$, distinct F-F bond distances are noticed in the loose-type $C_s$ NaF$_3$ corresponding to a NaF-F$_2$ complex. This has not been reported before, and particularly, it is almost degenerate (see relative energies in Figure 4) with the tight-type $C_s$ NaF$_3$ possessing closely balanced F-F bond distances. The tight-type $C_s$ NaF$_3$ has been previously reported using B3LYP$^9$ or CCSD(T)$^{10}$ methods. Although the NaF$_3$ structures are similar to those reported by Getmanskii and
coworkers, our CCSD(T)/AWCVTZ results are different from their CCSD(T)/6-311+G(3df) results, predicting both $C_s$ and $C_{2v}$ structures of LiF$_3$ and NaF$_3$ to be minima. This substantial inconsistency suggests that coupled-cluster results might be sensitive to the basis sets and/or dynamic correlation (frozen core) strategies selected for this specific system. The present CCSD(T)/AWCVTZ results for NaF$_3$ agree with Tozer and Sosa’s results, which predict the $C_s$ (both loose- and tight-type, Figure 4) and $C_{2v}$ NaF$_3$ to be two minima and a transition state, respectively, with an energy gap being 1 kcal/mol (our value: 0.6 kcal/mol) between the two. Unfortunately, no B3LYP results for LiF$_3$ were reported in the study by Tozer and Sosa. The splitting between the $C_s$ and $C_{2v}$ LiF$_3$ structures is 8.3 kcal/mol at the CCSD(T)/AWCVTZ level of theory in the present work. In addition, our attempt to locate a tight-type $C_s$ LiF$_3$ structure simply leads to the $C_{2v}$ structure.
Figure 4. Optimized structures and relative energies (ZPVE corrected) of the LiF$_3$ and NaF$_3$ stationary points at the CCSD(T)/AWCVTZ and MRCISD+Q(4e,3o)/AVTZ (in parentheses) levels of theory.

Unlike the $C_5$ structures in Figure 4, the $C_{2v}$ LiF$_3$ and NaF$_3$ are not “well-behaved” electronically with leading configurations falling below 90% (LiF$_3$: 76% and NaF$_3$: 83%, see SI for details) at the CASSCF(16e,10o)/AVTZ level of theory. The MRCISD+Q(4e,3o)/AVTZ optimization and frequency computations confirm the transition state nature of the $C_{2v}$ LiF$_3$ and NaF$_3$ geometries. Structural changes from the CCSD(T) to the MRCISD+Q method are not significant, as shown in Figure 4. The imaginary vibrational frequencies for $C_{2v}$ LiF$_3$ and NaF$_3$
are $146i$ and $13i$ ($32i$ cm$^{-1}$ using the AWCVQZ basis set) cm$^{-1}$ at the CCSD(T)/AWCVTZ level of theory, respectively. The corresponding MRCISD+Q(4e,3o)/AVTZ imaginary frequencies are $355i$ and $88i$ cm$^{-1}$, respectively, and the imaginary vibrational modes align with the CCSD(T) results.

Consistent with the IR/Raman experiments by Andrews, Riedel, and coworkers, our theoretical results do not support the formation of the symmetric T-shaped ($C_{2v}$) minima LiF$_3$ and NaF$_3$, which are actually transition states shown in Figure 4, through the MF + F$_2$ reactions. That is, no well-defined F$_3$ and its characteristic vibrations ($\nu_{as}$ and $\nu_s$) can be identified. However, are the three $C_s$ minima in Figure 4 stable enough to be detected by experiments? The endothermicities in Table 3 show that neutral dissociation of MF$_3$ into MF and F$_2$ is apparently favored over the ionic fragmentation ($M^+ + F_3^-$) due to the strong electrostatics between ions. The $D_0$ values ($\sim$3-6 kcal/mol) for MF$_3 \rightarrow$ MF + F$_2$ dissociation suggest that the MF$_3$ species are weakly bonded complexes. However, this does not entirely rule out their possible existence under low temperature ($\sim$15 K) experimental conditions by Andrews, Riedel, and coworkers. Unfortunately, no well-characterized LiF$_3$ (LiF + F$_2$) experimental vibrational spectra have been reported so far. Our harmonic vibrational frequencies for the $C_s$ LiF$_3$ complex (Figure 4)
are thus reported in Table 4 as genuine predictions, with the two highest frequencies (882 and 839 cm\(^{-1}\)) being perturbed Li-F and F-F bond stretches. The NaF\(_3\) vibrational spectra have been reported by Ault and Andrews.\(^\text{16}\) New infrared bands 455 and 460 cm\(^{-1}\) (a splitting) after the NaF + F\(_2\) reaction were assigned to a NaF-F\(_2\) complex, in which no F\(_3^-\) was formed. This seems to be consistent with our theoretical predictions. The harmonic frequencies 481 (tight-type NaF\(_3\)) and 497 (loose-type NaF\(_3\)) cm\(^{-1}\) in Table 4 are possible candidates, both of which correspond to Na-F bond stretches perturbed by the F\(_2\) moiety (experimental harmonic frequency\(^\text{34}\) for free NaF: 536 cm\(^{-1}\)). Because the two types of Cs NaF\(_3\) structure are nearly degenerate (Figure 4), this might be an explanation for the small splitting of the infrared bands (455 and 460 cm\(^{-1}\)).\(^\text{16}\)

**Table 3.** Endothermicities (\(D_0\), kcal/mol) of the dissociation processes for MF\(_3\) (M = Li, Na, K, Rb, and Cs) minima at the AE-CCSD(T)/AWCVTZ level of theory.

<table>
<thead>
<tr>
<th></th>
<th>(D_0 (\text{MF}_3 \rightarrow \text{MF} + \text{F}_2))</th>
<th>(D_0 (\text{MF}_3 \rightarrow \text{M}^+ + \text{F}_3^-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF(_3) (Cs)</td>
<td>2.7</td>
<td>162.9</td>
</tr>
<tr>
<td>NaF(_3) (Cs, loose-type)</td>
<td>4.2</td>
<td>134.5</td>
</tr>
<tr>
<td>NaF(_3) (Cs, tight-type)</td>
<td>4.1</td>
<td>134.5</td>
</tr>
<tr>
<td>KF(<em>3) (C(</em>{2v}))</td>
<td>5.9</td>
<td>121.4</td>
</tr>
<tr>
<td>RbF(<em>3) (C(</em>{2v}))</td>
<td>5.9</td>
<td>117.4</td>
</tr>
<tr>
<td>CsF(<em>3) (C(</em>{2v}))</td>
<td>4.0</td>
<td>113.1</td>
</tr>
<tr>
<td>CsF(_3) (Cs)</td>
<td>3.8</td>
<td>112.9</td>
</tr>
</tbody>
</table>
**Table 4.** Harmonic vibrational frequencies (cm\(^{-1}\)) and infrared intensities (km/mol, in parentheses) for the LiF\(_3\) and NaF\(_3\) minima at the CCSD(T)/AWCVTZ level of theory.

<table>
<thead>
<tr>
<th></th>
<th>LiF(_3) ((C_s))</th>
<th>NaF(_3) ((C_s), tight-type)</th>
<th>NaF(_3) ((C_s), loose-type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_1) ((a'))</td>
<td>882 (136)</td>
<td>481 (329)</td>
<td>617 (246)</td>
</tr>
<tr>
<td>(\omega_2) ((a'))</td>
<td>839 (13)</td>
<td>424 (101)</td>
<td>497 (54)</td>
</tr>
<tr>
<td>(\omega_3) ((a'))</td>
<td>224 (78)</td>
<td>350 (19)</td>
<td>238 (17)</td>
</tr>
<tr>
<td>(\omega_4) ((a'))</td>
<td>126 (7)</td>
<td>268 (327)</td>
<td>118 (170)</td>
</tr>
<tr>
<td>(\omega_5) ((a'))</td>
<td>70 (80)</td>
<td>78 (14)</td>
<td>56 (49)</td>
</tr>
<tr>
<td>(\omega_6) ((a''))</td>
<td>110 (23)</td>
<td>233 (2)</td>
<td>186 (4)</td>
</tr>
</tbody>
</table>

C. Heavy Alkali Metal Trifluorides: KF\(_3\), RbF\(_3\), and CsF\(_3\)

Unlike LiF\(_3\) and NaF\(_3\), the heavier alkali metal trifluorides (KF\(_3\), RbF\(_3\), and CsF\(_3\)) “\(M^+F_3^-\) ion pairs” can be effectively generated, and their vibrational spectra have been studied in detail\(^{11,12,15,16}\) as mentioned above. The results for the KF\(_3\), RbF\(_3\), and CsF\(_3\) minima at the CCSD(T)/AWCVTZ and MRCISD+Q(4e,3o)/AVTZ level of theory are shown in Figure 5.
Figure 5. Optimized structures and relative energies (ZPVE corrected) of the KF$_3$, RbF$_3$, and CsF$_3$ minima at the CCSD(T)/AECVTZ and MRCISD+Q(4e,3o)/AVTZ (in parentheses) level of theory.

Consistent with previous experiments and computations, the symmetric T-shaped ($C_{2v}$) KF$_3$, RbF$_3$, and CsF$_3$ minima are located. The F$_3^-$ moiety is slightly bent by ~20 degrees, and the bond distances are close to those reported in earlier studies using CCSD(T) methods. Attempts to locate the $C_s$ structures lead to the $C_{2v}$ structures, consistent with previous computations by Andrews, Riedel, and coworkers. A major difference, however, is a second $C_s$
minimum (nearly degenerate with the $C_{2v}$ structure, $\Delta E = 0.2$ kcal/mol, Figure 5) was found for CsF$_3$. Similar to the loose-type LiF$_3$ and NaF$_3$ (Figure 4), this new CsF$_3$ $C_s$ minimum corresponds to a CsF-F$_2$ complex with two distinct F-F bond distances (2.247 vs. 1.455 Å, Figure 5), but it is different from the $C_s$ CsF$_3$ minimum located with the PBE0/TZVP/ZORA method by Hoffmann and coworkers.$^{17}$ The latter possesses more nearly equal F-F bond distances (1.95 vs. 1.52 Å)$^{17}$ than the former. This inconsistency shows a sensitivity to the selected theoretical methods, although no significant multireference issues were found for either $C_s$ CsF$_3$ structure.

Similar to the $C_{2v}$ symmetry LiF$_3$ and NaF$_3$ structures, all heavy alkali metal trifluorides in $C_{2v}$ symmetry are not “well-behaved” electronically. The $C_{2v}$ KF$_3$, RbF$_3$, and CsF$_3$ molecules have leading configurations with weights of 83%, 85%, and 85%, respectively, at the CASSCF(16e,10o)/AVTZ level of theory. The MRCISD+Q(4e,3o)/AVTZ optimizations and frequency computations confirm the minimum nature of the three $C_{2v}$ species. As shown in Figure 5, the MRCISD+Q results basically align with the CCSD(T) geometries. Only small decreases in bond distances and angles can be found in going from the CCSD(T) to the MRCISD+Q method.

For the vibrational frequencies, typical F-F-F antisymmetric and symmetric stretch
frequencies of free F$_3^-$ and MF$_3$ (M = K, Rb, and Cs) are reported, together with the available experimental IR/Raman bands for comparison. The CCSD(T) and MRCISD+Q results are reported in Tables 5 and 6, respectively. For F$_3^-$, both antisymmetric and symmetric stretch frequencies using CCSD(T)/AWCVTZ are close to the experimental results from Riedel, Andrews, and coworkers.$^{3,11,12}$

For the antisymmetric stretch frequencies ($\nu_{as}$) of MF$_3$ (M = K, Rb, and Cs), CCSD(T) and MRCISD+Q, the harmonic frequencies basically align with each other, with the MRCISD+Q frequencies (Table 6) slightly higher than the former (Table 5). After the VPT2 anharmonic corrections, the CCSD(T) fundamental frequencies ($\nu_{as}$) are close to the experimental frequencies obtained in argon and neon matrices. Like the case of F$_3^-$, the CCSD(T) fundamental frequencies ($\nu_{as}$) are somewhat closer to the experimental frequencies in neon than to those measured in argon matrices.
### Table 5. Theoretical and experimental vibrational frequencies (cm\(^{-1}\)) of F\(_3^-\) and MF\(_3\) (M = K, Rb, and Cs) molecules at the CCSD(T)/AWCVTZ level of theory.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>F-F-F antisymmetric stretch ((v_{as}))</th>
<th>F-F-F symmetric stretch ((v_s))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>theory (harm)</td>
<td>theory (anhar)</td>
</tr>
<tr>
<td>F(<em>3^-) ((D</em>{\infty h}))</td>
<td>545</td>
<td>520</td>
</tr>
<tr>
<td>KF(<em>3) ((C</em>{2v}))</td>
<td>581</td>
<td>562</td>
</tr>
<tr>
<td>RbF(<em>3) ((C</em>{2v}))</td>
<td>583</td>
<td>569</td>
</tr>
<tr>
<td>CsF(<em>3) ((C</em>{2v}))</td>
<td>587</td>
<td>565</td>
</tr>
</tbody>
</table>

\(^a\) Anharmonic vibrational frequencies are obtained from the VPT2 computations. \(^b\) Ref. 3, 11, 12. \(^c\) Ref. 11. \(^d\) Ref. 12, 15, 16. \(^e\) Ref. 11. \(^f\) Ref. 11, 15, 16. \(^g\) Both 461 and 390 cm\(^{-1}\) Raman bands were observed in Ref. 15, 16. \(^h\) Ref. 11, 12, 15, 16.

### Table 6. Theoretical and experimental vibrational frequencies (cm\(^{-1}\)) of F\(_3^-\) and MF\(_3\) (M = K, Rb, and Cs) molecules at the MRCISD+Q(4e,3o)/AVTZ level of theory.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>F-F-F antisymmetric stretch ((v_{as}))</th>
<th>F-F-F symmetric stretch ((v_s))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>theory (harm)</td>
<td>expt (Ar)</td>
</tr>
<tr>
<td>F(<em>3^-) ((D</em>{\infty h}))</td>
<td>528</td>
<td>511(^b)</td>
</tr>
<tr>
<td>KF(<em>3) ((C</em>{2v}))</td>
<td>602</td>
<td>550(^d)</td>
</tr>
<tr>
<td>RbF(<em>3) ((C</em>{2v}))</td>
<td>590</td>
<td>550(^f)</td>
</tr>
<tr>
<td>CsF(<em>3) ((C</em>{2v}))</td>
<td>588</td>
<td>550(^h)</td>
</tr>
</tbody>
</table>

\(^a\) Only harmonic vibrational frequencies are obtained from the MRCISD+Q computations. \(^b\) Ref. 3, 11, 12. \(^c\) Ref. 11. \(^d\) Ref. 12, 15, 16. \(^e\) Ref. 11, 12. \(^f\) Ref. 11, 15, 16. \(^g\) Both 461 and 390 cm\(^{-1}\) Raman bands were observed in Ref. 15, 16. \(^h\) Ref. 11, 12, 15, 16.

For the symmetric stretch frequencies (\(v_s\)) of MF\(_3\) (M = K, Rb, and Cs), however, some
substantial differences can be found between CCSD(T) and MRCISD+Q results. The CCSD(T) harmonic frequencies (Table 5) are ~400 cm\(^{-1}\) and decrease to ~390 cm\(^{-1}\) with VPT2 anharmonic corrections. Significantly, the MRCISD+Q harmonic frequencies (~480 cm\(^{-1}\), Table 6) are much higher than the CCSD(T) values (by ~80 cm\(^{-1}\)) for all three \(C_{2v}\) MF\(_3\) (M = K, Rb, and Cs) species. Such large deviations of CCSD(T) from MRCISD+Q might be attributed to the lack of multireference treatment of the former, even though CCSD(T) shows a good performance in predicting the structures and antisymmetric stretch frequencies (\(\nu_{\text{as}}\)). According to previous experiments\(^{15, 16}\) and present theoretical results (Tables 5 and 6), RbF\(_3\) and CsF\(_3\) exhibit similar vibrational bands, so we will focus on the discussion of CsF\(_3\) here. The frequencies 461/389 cm\(^{-1}\) in Tables 5 and 6 correspond to the two Raman bands in the Ault and Andrews CsF + F\(_2\) \(\rightarrow\) CsF\(_3\) experiments.\(^{15, 16}\)

As discussed in the introduction, the 461 cm\(^{-1}\) band was suggested to be the true symmetric stretch frequencies (\(\nu_s\)) because of the disappearance of the 389 cm\(^{-1}\) band upon diffusion (15 K → 40 K → 15 K). In contrast, the 2015 paper by Riedel and coworkers\(^{11}\) assigned the 389 cm\(^{-1}\) band as \(\nu_s\) due to the identification of a possible \(\nu_{\text{as}} + \nu_s\) combination band (923 cm\(^{-1}\) in argon and 919 cm\(^{-1}\) in krypton) and its simultaneous disappearance with the 550 cm\(^{-1}\) \(\nu_{\text{as}}\) band upon
irradiation ($\lambda = 266$ nm). Which one, 461 or 389 cm$^{-1}$, is the true symmetric F-F-F stretch frequency in the CsF$_3$ vibrational spectra? Our CCSD(T)/AWCVTZ results for $\nu_s$ (harmonic: 396 cm$^{-1}$ & anharmonic: 384 cm$^{-1}$, Table 5) agree well with the 389 cm$^{-1}$ Raman band,\textsuperscript{15,16} consistent with the CCSD(T)/def2-QZVPP value ($\nu_s = 388$ cm$^{-1}$, anharmonic) in the 2015 paper by Andrews, Riedel, and coworkers.\textsuperscript{12} However, our MRCISD+Q(4e,3o)/AVTZ result for $\nu_s$ is 478 cm$^{-1}$ (harmonic, Table 6). This harmonic frequency is expected to be further lowered and getting close to the 461 cm$^{-1}$ Raman band, if the anharmonic correction can be included. Thus, the MRCISD+Q(4e,3o)/AVTZ result supports the 461 cm$^{-1}$ band as the F-F-F symmetric stretch frequencies, rather than the 389 cm$^{-1}$ band which appears simultaneously with the former in the Ault and Andrews Raman spectra.\textsuperscript{15,16}

To further examine the symmetric stretch frequency ($\nu_s$), several additional coupled-cluster and multireference computations were performed for CsF$_3$, and the results are listed in Table 7. Although with small deviations, all coupled-cluster [CCSD(T), CCSDT, and CCSDT(Q)] results support Riedel’s recent assignment (389 cm$^{-1}$)\textsuperscript{11} for the $\nu_s$ of CsF$_3$. On the contrary, the multireference (CASPT2, CASPT3, and MRCISD+Q) results predict higher $\nu_s$ frequencies which support the original assignment of $\nu_s$ (461 cm$^{-1}$) by Ault and Andrews.\textsuperscript{15,16} In general, the
multireference methods tend to predict slightly smaller F-F (but longer Cs-F bond distances) than those from coupled-cluster methods. However, the difference is not substantial. Specifically, the differences in bond distances between CCSDT(Q) and MRCISD+Q(4e,3o) are ~0.03 and ~0.01 Å for the F-F and Cs-F distances, respectively, while the difference in the F-F-F angle is only 1 degree.

Table 7. The structures and harmonic F-F-F symmetric stretch frequencies (ω_s, cm\(^{-1}\)) of the C\(_{2v}\) CsF\(_3\) at higher levels of theory.

<table>
<thead>
<tr>
<th>Theoretical level(^a)</th>
<th>D(F-F)(^b)</th>
<th>D(Cs-F)(^b)</th>
<th>∠(F-F-F)(^c)</th>
<th>ω_s (F-F-F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCSD(T)/AVTZ</td>
<td>1.747</td>
<td>2.572</td>
<td>162</td>
<td>398</td>
</tr>
<tr>
<td>CCSDT/AVTZ</td>
<td>1.741</td>
<td>2.574</td>
<td>162</td>
<td>415</td>
</tr>
<tr>
<td>CCSDT(Q)/AVTZ</td>
<td>1.759</td>
<td>2.573</td>
<td>162</td>
<td>385</td>
</tr>
<tr>
<td>CASPT2(4e,3o)/AVTZ</td>
<td>1.746</td>
<td>2.574</td>
<td>162</td>
<td>526</td>
</tr>
<tr>
<td>CASPT3(4e,3o)/AVTZ</td>
<td>1.713</td>
<td>2.586</td>
<td>163</td>
<td>515</td>
</tr>
<tr>
<td>MRCISD+Q(4e,3o)/AVTZ</td>
<td>1.727</td>
<td>2.581</td>
<td>163</td>
<td>478</td>
</tr>
</tbody>
</table>

\(^a\) Both optimization and frequencies were performed at each level of theory.
\(^b\) Distance (D) in Angstroms.
\(^c\) Angles (∠) in degrees.

The combination band (923 cm\(^{-1}\) in Ar and 919 cm\(^{-1}\) in Kr) has been assigned to the combination of \(ν_{as}\) and \(ν_s\) (550 + 389 = 939 cm\(^{-1}\)) by Riedel and coworkers.\(^{11}\) However, if the true \(ν_s\) of CsF\(_3\) is 461 cm\(^{-1}\) (as supported by the multireference computations), what could be the alternative origin of this combination band? The vibrational frequencies of the two CsF\(_3\) minima
(C$_{2v}$ and C$_s$, Figure 5) are reported in Table 8. It is possible to obtain this combination band from the 588 and 347 cm$^{-1}$ bands (harmonic: 588 + 347 = 935 cm$^{-1}$) of C$_{2v}$ CsF$_3$. It might also come from the 748 and 178 cm$^{-1}$ bands (harmonic: 748 + 178 = 926 cm$^{-1}$) of the newly located C$_s$ CsF$_3$. The actual frequency should be lower than those values because of anharmonicity. Moreover, due to the near degeneracy (0.2 kcal/mol, Figure 5) of the C$_{2v}$ and C$_s$ CsF$_3$ minima, the simultaneous disappearance of the two different species upon irradiation ($\lambda = 266$ nm)$^{11}$ could occur. Therefore, treating the simultaneous disappearance of the 550 and 923 cm$^{-1}$ bands as solid evidence to verify the F-F-F symmetric stretch frequency $\nu_s$ might need to be reconsidered, because they could come from different species. Those additional possibilities certainly complicate the band assignment, and future studies should revisit this problem.

Table 8. Vibrational frequencies (cm$^{-1}$) of the C$_{2v}$ and C$_s$ CsF$_3$ minima.

<table>
<thead>
<tr>
<th></th>
<th>CsF$<em>3$ (C$</em>{2v}$)$^a$</th>
<th>description$^c$</th>
<th>CsF$_3$ (C$_s$)$^b$</th>
<th>description$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_1$ ($a_1$)</td>
<td>478</td>
<td>$\nu_s$(F$_3$)</td>
<td>$\nu_1$ ($a'$)</td>
<td>748</td>
</tr>
<tr>
<td>$\omega_2$ ($a_1$)</td>
<td>347</td>
<td>$\delta$(F$_3$)/$\nu$(CsF)</td>
<td>$\nu_2$ ($a'$)</td>
<td>330</td>
</tr>
<tr>
<td>$\omega_3$ ($a_1$)</td>
<td>173</td>
<td>$\delta$(F$_3$)</td>
<td>$\nu_3$ ($a'$)</td>
<td>178</td>
</tr>
<tr>
<td>$\omega_4$ ($b_1$)</td>
<td>240</td>
<td>$\gamma$(F$_3$)</td>
<td>$\nu_4$ ($a'$)</td>
<td>127</td>
</tr>
<tr>
<td>$\omega_5$ ($b_2$)</td>
<td>588</td>
<td>$\nu_{as}$(F$_3$)</td>
<td>$\nu_5$ ($a'$)</td>
<td>44</td>
</tr>
<tr>
<td>$\omega_6$ ($b_2$)</td>
<td>104</td>
<td>$\rho$(F$_3$)</td>
<td>$\nu_6$ ($a''$)</td>
<td>160</td>
</tr>
</tbody>
</table>

$^a$ MRCISD+Q(4e,3o)/AVTZ harmonic frequencies. $^b$ CCSD(T)/AWCVTZ harmonic frequencies. $^c$ $\nu$: stretch; $\delta$: bend; $\rho$: rock; $\gamma$: out-of-plane bend; $as$: antisymmetric; $s$: symmetric.
Conclusions

The alkali metal trifluorides MF$_3$ (M = Li, Na, K, Rb, and Cs) are challenging molecular systems for both experimental and theoretical studies. The most important challenges include determination of the genuine MF$_3$ minima and the global minima, the problematic existence of the light alkali metal trifluorides MF$_3$ (M = Li and Na), and the assignment of the F-F-F symmetric stretch frequencies for the heavy alkali metal trifluorides MF$_3$ (M = K, Rb, and Cs).

In the present study, we provide new explanations and solutions to the above problems using very high level coupled-cluster [CCSD(T), CCSDT, and CCSDT(Q)] and multireference (CASPT2, CASPT3, and MRCISD+Q) methods. Benchmarks show good performance of the coupled-cluster method [CCSD(T)/AWCVTZ, see Methods] in predicting reliable structures, harmonic frequencies, and endothermicities for the selected test set. The CASPT2 and MRCISD+Q methods were applied for those structures with multireference issues (all $C_{2v}$ structures), and the corresponding results mostly align with the CCSD(T) results.

For locating the true MF$_3$ minima and global minima, the results support a preference of $C_s$
minima for MF$_3$ (M = Li and Na) and $C_{2v}$ minima for MF$_3$ (M = K, Rb, and Cs). Comparison with earlier theoretical studies exhibit a strong method-dependence in determining the nature of the species (transition states or minima) and the energy difference between isomers (locating global minima). The CCSD(T) results were found to be sensitive to different basis sets, frozen core options, and dynamic correlation types. For the species where multiple minima were located, the near degeneracies of those minima can be found in most cases, according to the CCSD(T) results.

Concerning the existence of MF$_3$ (M = Li and Na), the endothermicities (~3-4 kcal/mol) for the favored MF$_3$ $\rightarrow$ MF + F$_2$ neutral fragmentation suggest that the MF$_3$ (M = Li and Na) structures are weakly bonded complexes. Their existence at low temperatures cannot be ruled out. Vibrational frequency analysis suggests possible candidates to match the previously assigned NaF$_3$ IR bands. Because no well-characterized LiF$_3$ vibrational spectra have been reported so far, its computed vibrational frequencies are a challenge to future experiments.

For the F-F-F symmetric stretch frequencies ($\nu_s$) of MF$_3$ (M = K, Rb, and Cs), striking differences were found between the CCSD(T) and MRCISD+Q results, even though the former shows a good performance in predicting most structures and antisymmetric stretch frequencies
(ν₃). The very high coupled-cluster [CCSDT and CCSDT(Q)] results agree with the recent reassignment [389 cm⁻¹, RSC Adv. 2015, 5, 106568] of ν₃ for CsF₂, while the multireference (CASPT2, CASPT3, and MRCISD+Q) results support the original assignment of ν₃ [461 cm⁻¹, J. Am. Chem. Soc. 1976, 98, 1591; Inorg. Chem. 1977, 16, 2024]. The F-F-F symmetric stretch frequencies for MF₃ (M = K, Rb, and Cs) continue to be an experimental and theoretical challenge. For the time being, the application of even higher level theoretical methods will be difficult. New experiments are strongly encouraged.

**Supporting Information**

Detailed information of all species at different levels of theory and multireference diagnostic are available in the Supporting Information.

**Conflicts of Interest**

There are no conflicts of interest to declare.
Acknowledgments

This research was supported by the U.S. National Science Foundation, Grant No. CHE-1661604.

References


MF₃ (M = K, Rb, and Cs)

*symmetric stretch frequency*

νₛ (389 or 461 cm⁻¹?)

The mysterious F-F-F symmetric stretch frequencies for the MF₃ molecules continue to provide a great challenge to theory and experiment.