Vibrational Frequencies, Structures, and Energetics of the Highly Challenging Alkali Metal Trifluorides MF_3 (M = Li, Na, K, Rb, and Cs)

Journal:	*Physical Chemistry Chemical Physics*
Manuscript ID	CP-ART-05-2018-003434.R1
Article Type:	Paper
Date Submitted by the Author:	29-Jun-2018
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 MF_3 (M = Li, Na, K, Rb, and Cs)

Zhi Sun and Henry F. Schaefer III*

Center for Computational Quantum Chemistry, University of Georgia

Athens, Georgia 30602, USA

**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 $MF_3 \rightarrow MF + F_2$ 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 (ν_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 (ν_{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 ν_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 F_3^- is a highly challenging system for theoretical studies. Single-reference methods including DFT,[1-4] MP*n* (n = 2, 3, or 4),[2, 3, 5] configuration interaction (CI),[2, 5] and coupled-cluster (CC)[3, 5] produce largely inconsistent results for the structure, binding energy, and vibrational frequencies of 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)].[6] Theoretical results are also sensitive to the selection of active space, basis sets, and dynamic correlation.[1, 6]

The challenges associated with 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)

$$\underset{\text{(I)}}{F:F \quad F^{-}} \qquad\qquad \underset{\text{(II)}}{F^{-} \quad F:F} \qquad\qquad \underset{\text{(III)}}{F^{\bullet} \quad F^{-} \quad F^{\bullet}}$$

Figure 1. Valence-bond structures most often proposed for F_3^-.

contributes significantly to the F_3^- electronic structure, according to the 2004 valence bond (VB) study of Braïda and Hiberty.[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• at high collision energies, instead of $F_2 + F^-$.[8]

Significant challenges remain for theoretical studies of the interactions between F_3^- and the alkali metal cations (M^+, M = Li, Na, K, Rb, 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.[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[13] and a recent theoretical study.[14]

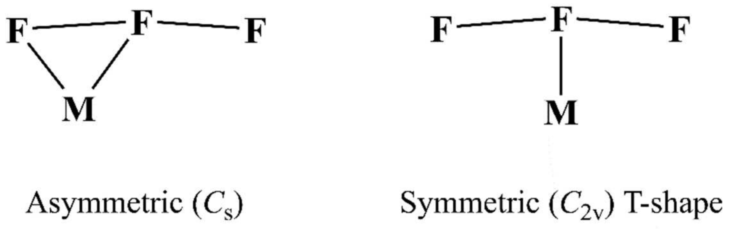


Figure 2. Two isomers of MF_3 (M = Li, Na, K, Rb, and Cs) reported in the literature.

An early systematic study by Tozer and Sosa[9] found that Hartree-Fock, MP2, QCISD, BLYP, and B3LYP give inconsistent results in their predictions of the MF_3 structures. Only the B3LYP functional reasonably predicts the metal-dependent minima (C_s NaF_3; C_{2v} KF_3, RbF_3, and CsF_3, see Figure 2) align with the results inferred from the IR/Raman spectra by Ault and Andrews.[15, 16] The C_{2v} minima for KF_3 and CsF_3 were recently (2015) predicted at the CCSD(T)/def2-QZVPP level of theory by Andrews, Riedel and coworkers.[12] The C_s symmetry KF_3 and CsF_3 structures were not reported there because the C_s structures (see Figure 2) were selected as the initial geometries for optimization which lead to the C_{2v} minima. In contrast, in the same year (2015), Hoffmann and coworkers located the C_s CsF_3 structure as a minimum with the PBE0/TZVP/ZORA method, whereas the C_{2v} CsF_3 structure was found to be a transition state connecting the two equivalent C_s CsF_3 structures with a small barrier of ~1 kcal/mol.[17] Another paper, published in 2015 by Getmanskii and coworkers, mainly focuses on MF_3 with light alkali metals (M = Li, Na, and K).[10] Apparently Getmanskii disagrees with the B3LYP results from Tozer and Sosa,[9] because both C_s 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.[11, 12, 15, 16] According to the early experiments by Andrews and coworkers,[15, 16] only large alkali metals cations (K^+, Rb^+, and Cs^+) can effectively form stable $M^+F_3^-$ "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 (ν_{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 (ν_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 → 40 K → 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 ν_s. Therein Riedel's logic is that, except for the 550 cm^{-1} ν_{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 ν_{as} and ν_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} ν_{as} band upon irradiation ($\lambda = 266$ nm), suggesting the two might belong to the same species. If this is true, the previously computed ν_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 ν_s.

Last but not least, previous experiments suggest that the $M^+F_3^-$ "ion pair" with the light alkali metals (Li and Na) cannot be effectively produced through the MF + 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 MF + 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 $Na^{+}F^{-}\cdots F_2$ 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} 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: 2*p*, Li: 2*s*, Na: 3*s*, K: 4*s*, Rb: 5*s*, and Cs: 6*s*) 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 CsF_3, which will be discussed later.

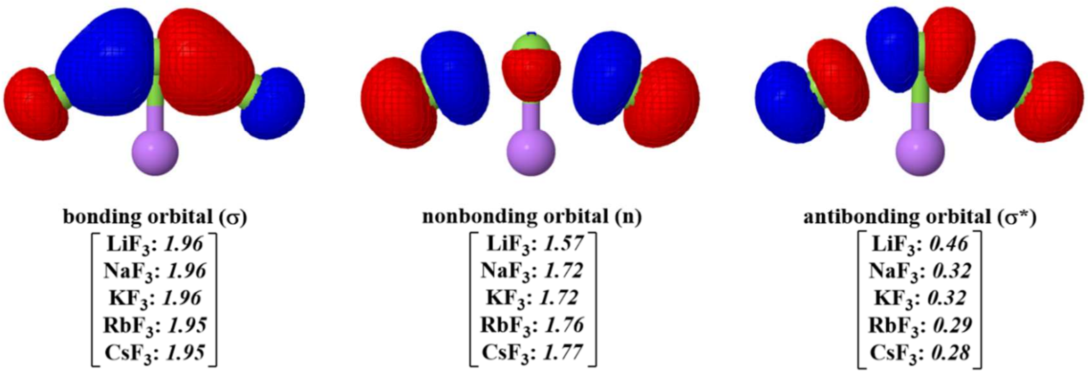


Figure 3. Orbitals (illustrated for LiF_3) included in the MRCISD+Q(4e,3o)/AVTZ computations for C_{2v} MF_3 (M = Li, Na, K, Rb, and Cs) with natural orbital occupation numbers (in brackets) obtained at the CASSCF(16e,10o)/AVTZ level of theory.

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 F_2 are chosen as a test set because the experimental information on the tetra-atomic MF_3 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.[34] 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 F_2 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 F_2 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 F_2 (M = Li, Na, K, Rb, and Cs) molecules, against experimental values compiled by Huber and Herzberg (Ref. 34).

Equilibrium Bond Lengths					Harmonic Vibrational Frequencies		
Species	Computed	Experiment	Deviation	Percent Error	Computed	Experiment	Percent Error
LiF	1.569	1.564	0.005	0.3%	905	910	0.5%
NaF	1.934	1.926	0.008	0.4%	531	536	0.9%
KF	2.183	2.172	0.011	0.5%	424	428	0.9%
RbF	2.286	2.270	0.016	0.7%	372	376	1.1%
CsF	2.371	2.345	0.026	1.1%	345	353	2.3%
F_2	1.417	1.412	0.005	0.4%	918	917	0.1%
		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.[2] 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.

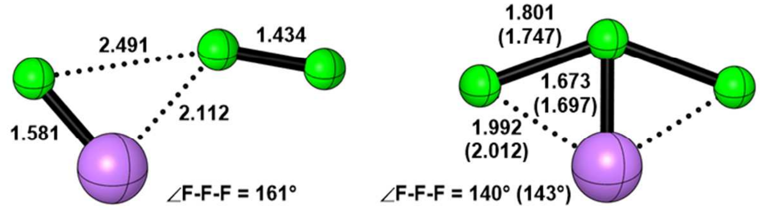
	Theory (present work)	Experiment (ref. 2)
D_0 ($F_3^- \rightarrow F_2 + F^-$)	22.7 kcal/mol	1.02 ± 0.11 eV (~23.5 kcal/mol)
D_0 ($F_3^- \rightarrow F + F_2^-$)	31.3 kcal/mol	1.30 ± 0.13 eV (~30.0 kcal/mol)

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) results.

B. Light Alkali Metal Trifluorides: LiF_3 and NaF_3

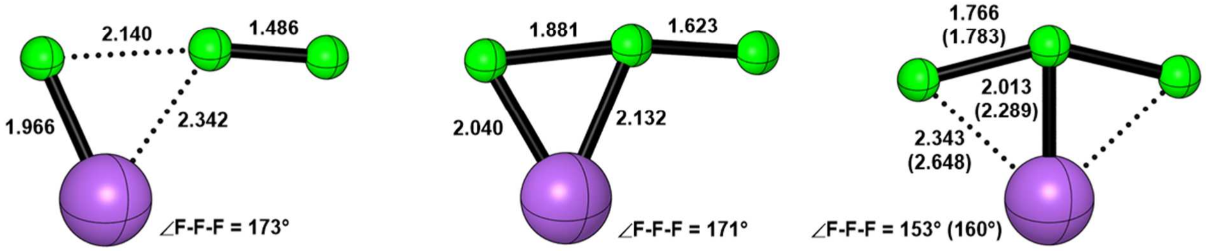
The results for light alkali metal trifluorides (LiF_3 and NaF_3) at the CCSD(T)/AWCVTZ and MRCISD+Q(4e,3o)/AVTZ levels of theory are shown in Figures 4. As discussed in the Introduction, one major challenge for previous theoretical studies of MF_3 is to determine which structure (C_s or C_{2v}) in Figure 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,[10] 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.[9] 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.



LiF_3 (C_s, $^1A'$)
(0.0 kcal/mol, minimum)

LiF_3 (C_{2v}, $^1A_1$)
(8.3 kcal/mol, transition state)



NaF_3 (C_s, $^1A'$, loose)
(0.0 kcal/mol, minimum)

NaF_3 (C_s, $^1A'$, tight)
(0.0 kcal/mol, minimum)

NaF_3 (C_{2v}, $^1A_1$)
(0.6 kcal/mol, transition state)

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_s 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 146*i* and 13*i* (32*i* 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 355*i* and 88*i* 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,[11, 12, 15, 16] 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 (ν_{as} and ν_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 (~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 (~15 K) experimental conditions by Andrews, Riedel, and coworkers.[11, 12, 15, 16] 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.[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[34] for free NaF: 536 cm^{-1}). Because the two types of C_s 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}).[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.

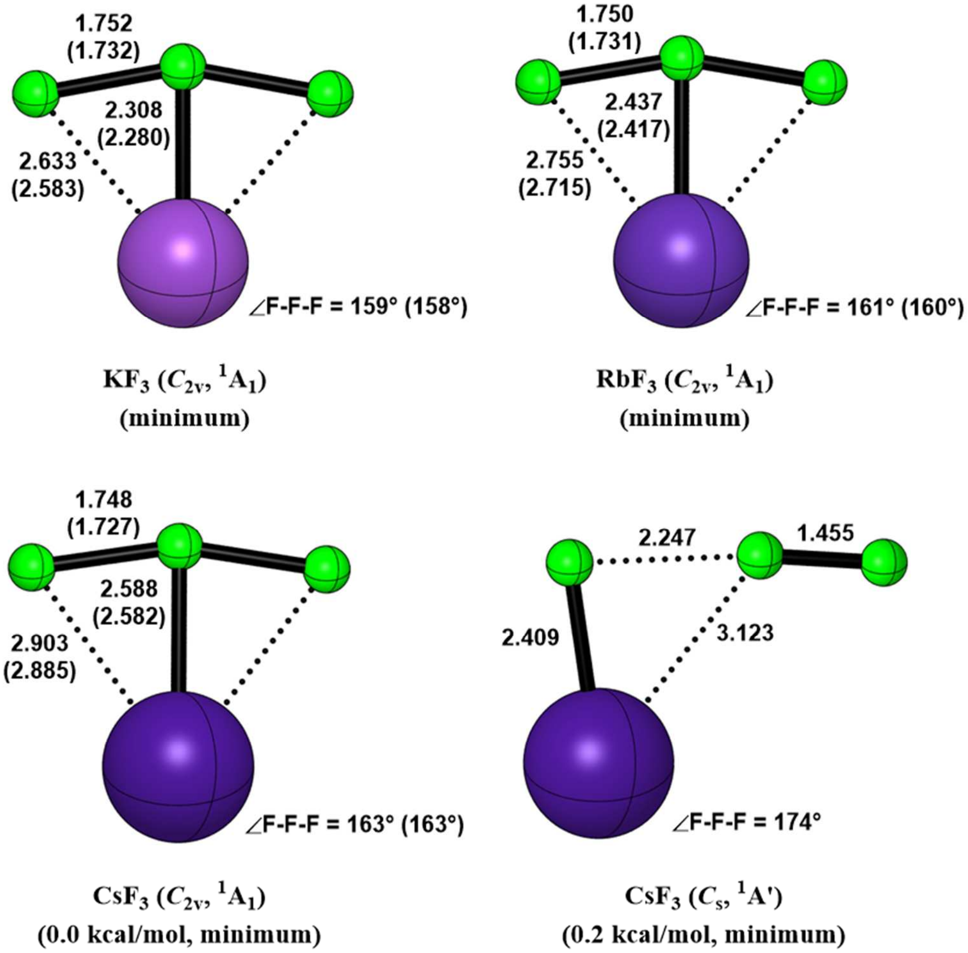
	D_0 ($MF_3 \rightarrow MF + F_2$)	D_0 ($MF_3 \rightarrow M^+ + F_3^-$)
LiF_3 (C_s)	2.7	162.9
NaF_3 (C_s, loose-type)	4.2	134.5
NaF_3 (C_s, tight-type)	4.1	134.5
KF_3 (C_{2v})	5.9	121.4
RbF_3 (C_{2v})	5.9	117.4
CsF_3 (C_{2v})	4.0	113.1
CsF_3 (C_s)	3.8	112.9

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.

	LiF_3 (C_s)	NaF_3 (C_s, tight-type)	NaF_3 (C_s, loose-type)
ω_1 (a')	882 (136)	481 (329)	617 (246)
ω_2 (a')	839 (13)	424 (101)	497 (54)
ω_3 (a')	224 (78)	350 (19)	238 (17)
ω_4 (a')	126 (7)	268 (327)	118 (170)
ω_5 (a')	70 (80)	78 (14)	56 (49)
ω_6 (a'')	110 (23)	233 (2)	186 (4)

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.



KF_3 (C_{2v}, $^1A_1$)
(minimum)

RbF_3 (C_{2v}, $^1A_1$)
(minimum)

CsF_3 (C_{2v}, $^1A_1$)
(0.0 kcal/mol, minimum)

CsF_3 (C_s, $^1A'$)
(0.2 kcal/mol, minimum)

Figure 5. Optimized structures and relative energies (ZPVE corrected) of the KF_3, RbF_3, and CsF_3 minima at the CCSD(T)/AWCVTZ and MRCISD+Q(4e,3o)/AVTZ (in parentheses) level of theory.

Consistent with previous experiments and computations,[9-12, 15, 16] 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.[10, 12] Attempts to locate the C_s structures lead to the C_{2v} structures, consistent with previous computations by Andrews, Riedel, and coworkers.[12] A major difference, however, is a second C_s

minimum (nearly degenerate with the C_{2v} structure, ΔE = 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 (v_{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 (v_{as}) are close to the experimental frequencies obtained in argon and neon matrices. Like the case of F_3^-, the CCSD(T) fundamental frequencies (v_{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]

	F-F-F antisymmetric stretch (ν_{as})				F-F-F symmetric stretch (ν_s)			
	theory (harm)	theory (anharm)	expt (Ar)	expt (Ne)	theory (harm)	theory (anharm)	expt (Ar)	expt (Kr)
F_3^- ($D_{\infty h}$)	545	520	511[b]	525[b]	399	388	396 ± 5[c]	394 ± 5[c]
KF_3 (C_{2v})	581	562	550[d]	561[e]	405	397	–	–
RbF_3 (C_{2v})	583	569	550[f]	561[c]	398	390	(460/390)[g]	–
CsF_3 (C_{2v})	587	565	550[h]	561[e]	396	384	(461/389)[g]	388 ± 5[c]

[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, 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.

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]

	F-F-F antisymmetric stretch (ν_{as})			F-F-F symmetric stretch (ν_s)		
	theory (harm)	expt (Ar)	expt (Ne)	theory (harm)	expt (Ar)	expt (Kr)
F_3^- ($D_{\infty h}$)	528	511[b]	525[b]	417	396 ± 5[c]	394 ± 5[c]
KF_3 (C_{2v})	602	550[d]	561[e]	488	–	–
RbF_3 (C_{2v})	590	550[f]	561[c]	481	(460/390)[g]	–
CsF_3 (C_{2v})	588	550[h]	561[e]	478	(461/389)[g]	388 ± 5[c]

[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 (ν_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 (ν_{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 (ν_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 ν_s due to the identification of a possible $\nu_{as} + \nu_s$ combination band (923 cm^{-1} in argon and 919 cm^{-1} in krypton) and its simultaneous disappearance with the 550 cm^{-1} ν_{as} band upon irradiation (λ = 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 v_s (harmonic: 396 cm^{-1} & anharmonic: 384 cm^{-1}, Table 5) agree well with the 389 cm^{-1} Raman band,[15, 16] consistent with the CCSD(T)/def2-QZVPP value (v_s = 388 cm^{-1}, anharmonic) in the 2015 paper by Andrews, Riedel, and coworkers.[12] However, our MRCISD+Q(4e,3o)/AVTZ result for v_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.[15, 16]

To further examine the symmetric stretch frequency (v_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})[11] for the v_s of CsF_3. On the contrary, the multireference (CASPT2, CASPT3, and MRCISD+Q) results predict higher v_s frequencies which support the original assignment of v_s (461 cm^{-1}) by Ault and Andrews.[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.

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

[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 (λ = 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 v_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.

	CsF_3 (C_{2v})[a]	description[c]		CsF_3 (C_s)[b]	description[c]
ω_1 (a_1)	478	$v_s(F_3)$	v_1 (a')	748	$v(F_2)$
ω_2 (a_1)	347	$\delta(F_3)/v(CsF)$	v_2 (a')	330	$v(CsF)$
ω_3 (a_1)	173	$\delta(F_3)$	v_3 (a')	178	$\delta(F_3)$
ω_4 (b_1)	240	$\gamma(F_3)$	v_4 (a')	127	$v(F_2)$
ω_5 (b_2)	588	$v_{as}(F_3)$	v_5 (a')	44	$\delta(CsF_2)$
ω_6 (b_2)	104	$\rho(F_3)$	v_6 (a'')	160	$\gamma(F_3)$

[a] MRCISD+Q(4e,3o)/AVTZ harmonic frequencies. [b] CCSD(T)/AWCVTZ harmonic frequencies. [c] v: stretch; δ: bend; ρ: rock; γ: 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 (ν_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

(ν_{as}). The very high coupled-cluster [CCSDT and CCSDT(Q)] results agree with the recent reassignment [389 cm^{-1}, *RSC Adv.* **2015**, *5*, 106568] of ν_s for CsF_3, while the multireference (CASPT2, CASPT3, and MRCISD+Q) results support the original assignment of ν_s [461 cm^{-1}, *J. Am. Chem. Soc.* **1976**, *98*, 1591; *Inorg. Chem.* **1977**, *16*, 2024]. The F-F-F symmetric stretch frequencies for MF_3 (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

(1) Malcolm, N. O. J.; McDouall, J. J. W. *J. Phys. Chem.* **1996**, *100*, 10131-10134.

(2) Artau, A.; Nizzi, K. E.; Hill, B. T.; Sunderlin, L. S.; Wenthold, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 10667-10670.

(3) Riedel, S.; Köchner, T.; Wang, X.; Andrews, L. *Inorg. Chem.* **2010**, *49*, 7156-7164.

(4) Gutsev, G. L.; Belay, K. G.; Weatherford, C. A.; Ramachandran, B. R.; Gutsev, L. G.; Jena, P. *J. Phys. Chem. A* **2015**, *119*, 6483-6492.

(5) Heard, G. L.; Marsden, C. J.; Scuseria, G. E. *J. Phys. Chem.* **1992**, *96*, 4359-4366.

(6) Mota, F.; Novoa, J. J. *J. Chem. Phys.* **1996**, *105*, 8777-8784.

(7) Braïda, B.; Hiberty, P. C. *J. Am. Chem. Soc.* **2004**, *126*, 14890-14898.

(8) Tuinman, A. A.; Gakh, A. A.; Hinde, R. J.; Compton, R. N. *J. Am. Chem. Soc.* **1999**, *121*, 8397-8398.

(9) Tozer, D. J.; Sosa, C. P. *Mol. Phys.* **1997**, *90*, 515-524.

(10) Getmanskii, I. V.; Koval, V. V.; Minyaev, R. M.; Minkin, V. I. *Mendeleev Commun.* **2015**, *25*, 417-419.

(11) Redeker, F. A.; Beckers, H.; Riedel, S. *RSC Adv.* **2015**, *5*, 106568-106573.

(12) Vent-Schmidt, T.; Brosi, F.; Metzger, J.; Schlöder, T.; Wang, X.; Andrews, L.; Müller, C.; Beckers, H.; Riedel, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 8279-8283.

(13) Ault, B. S.; Andrews, L. *J. Chem. Phys.* **1976**, *64*, 4853-4859.

(14) Sun, Z.; Moore, K. B.; Hill, J. G.; Peterson, K. A.; Schaefer, H. F.; Hoffmann, R. *J. Phys. Chem. B* **2018**, *122*, 3339–3353.

(15) Ault, B. S.; Andrews, L. *J. Am. Chem. Soc.* **1976**, *98*, 1591-1593.

(16) Ault, B. S.; Andrews, L. *Inorg. Chem.* **1977**, *16*, 2024-2028.

(17) Rogachev, A. Y.; Miao, M. S.; Merino, G.; Hoffmann, R. *Angew. Chem. Int. Ed.* **2015**, *54*, 8275-8278.

(18) Crawford, T. D.; Schaefer, H. F., in *Reviews in Computational Chemistry, Vol 14*, edited by K. B. Lipkowitz, and D. B. Boyd (Wiley-VCH, Inc, New York, 2000), pp. 33-136.

(19) Shavitt, I.; Bartlett, R. J., *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (Cambridge University Press, Cambridge, 2009), Cambridge Molecular Science.

(20) Harding, M. E.; Metzroth, T.; Gauss, J.; Auer, A. A. *J. Chem. Theory Comput.* **2008**, *4*, 64-74.

(21) CFOUR, a quantum chemical program package by Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G. with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Cheng, L.; Christiansen, O.; Heckert, M.; Heun, O.; *et al.*, and the integral packages *MOLECULE* (Almlöf, J. and Taylor, P. R.), *PROPS* (Taylor, P. R.), *ABACUS* (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; and Olsen, J.), and ECP routines by Mitin, A. V. and van Wüllen, C. For the current version see, http://www.cfour.de.

(22) Hill, J. G.; Peterson, K. A. *J. Chem. Phys.* **2017**, *147*, 244106.

(23) Peterson, K. A.; Dunning Jr., T. H. *J. Chem. Phys.* **2002**, *117*, 10548-10560.

(24) Lim, I. S.; Schwerdtfeger, P.; Metz, B.; Stoll, H. *J. Chem. Phys.* **2005**, *122*, 104103.

(25) Clabo, D. A.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F. *Chem. Phys.* **1988**, *123*, 187-239.

(26) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Györffy, W.; Kats, D.; Korona, T.; Lindh, R. *et al.*, MOLPRO, version 2010.1, a package of *ab initio* programs, see http://www.molpro.net.

(27) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514-522.

(28) Werner, H. J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803-5814.

(29) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem* **1974**, *8*, 61-72.

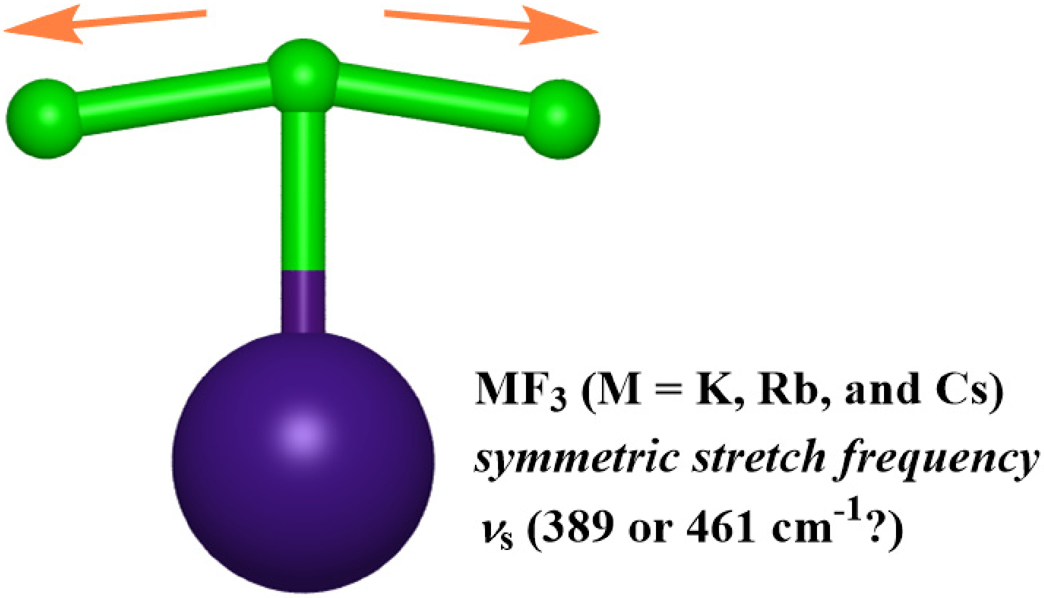
(30) Prascher, B. P.; Woon, D. E.; Peterson, K. A.; Dunning, T. H.; Wilson, A. K. *Theor. Chem. Acc.* **2011**, *128*, 69-82.

(31) Dunning Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007-1023.

(32) Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645-661.

(33) Celani, P.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 5546-5557.

(34) Huber, K. P.; Herzberg, G., *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).



The mysterious F-F-F symmetric stretch frequencies for the MF_3 molecules continue to provide a great challenge to theory and experiment.