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Electronic Supplementary Information

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

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1. Optimized geometries and harmonic frequencies at the AE-CCSD(T)/AWCVTZ level of theory

LiF

Coordinates of optimized geometry:

F
Li 1 B1

B1 = 1.568526332545583

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 σ_g^+ 905 (152)

NaF

Coordinates of optimized geometry:

F
Na 1 B1

B1 = 1.933910268288291

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 σ_g^+ 531 (70)

KF

Coordinates of optimized geometry:

F
K 1 B1

B1 = 2.182622917421423

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 σ_g^+ 424 (105)

RbF

Coordinates of optimized geometry:

F
Rb 1 B1

B1 = 2.285576516424454

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 σ_g^+ 372 (108)

CsF

Coordinates of optimized geometry:

F
Cs 1 B1

B1 = 2.371104340231122

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 σ_g^+ 345 (136)

F_2

Coordinates of optimized geometry:

F
F 1 B1

B1 = 1.416904627285431

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 σ_g^+ 918 (0)

F_3^-

Coordinates of optimized geometry:

F
F 1 B1
X 1 B2 2 A1
F 1 B1 3 A2 2 D1

B1 = 1.737442649354848
B2 = 2.000000000000000
A1 = 90.000000000000000
A2 = 90.000000000000000
D1 = -180.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 σ_g^+ 399 (0)
ω_2 σ_g^- 545 (932)
ω_3 π_u 256 (49)
ω_4 π_u 256 (49)

LiF_3 (C_s, $^1A'$): minimum

Coordinates of optimized geometry:

F
F 1 B1
F 2 B2 1 A2
Li 3 B3 2 A3 1 D3

B1 = 1.433459972396837
B2 = 2.491412348924244
A2 = 160.984768103193318
B3 = 1.580603483638631
A3 = 57.372341489243531
D3 = 0.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 a' 882 (136)
ω_2 a' 839 (13)
ω_3 a' 224 (78)
ω_4 a' 126 (7)
ω_5 a' 70 (80)
ω_6 a'' 110 (23)

LiF_3 (C_{2v}, $^1A_1$): transition state

Coordinates of optimized geometry:

Li
F 1 B1
F 2 B2 1 A2
F 2 B2 1 A2 3 D3

B1 = 1.672718919476552
B2 = 1.800716098370120
A2 = 69.889224503827677
D3 = 180.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 a_1 723 (101)
ω_2 a_1 364 (1)
ω_3 a_1 172 (18)
ω_4 b_1 199 (32)
ω_5 b_2 530 (45)
ω_6 b_2 146*i* (9)

NaF_3 (C_s, $^1A'$, loose-type): minimum

Coordinates of optimized geometry:

F
F 1 B1
F 2 B2 1 A2
Na 3 B3 2 A3 1 D3

B1 = 1.485633875264730
B2 = 2.139592247668878

A2 = 172.807096080481159
B3 = 1.965899349108170
A3 = 69.430579159113520
D3 = 0.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 *a*' 617 (247)
ω_2 *a*' 497 (54)
ω_3 *a*' 238 (17)
ω_4 *a*' 118 (170)
ω_5 *a*' 56 (49)
ω_6 *a*'' 186 (4)

NaF_3 (C_s, $^1A'$, tight-type): minimum

Coordinates of optimized geometry:

F
F 1 B1
F 2 B2 1 A2
Na 3 B3 2 A3 1 D3

B1 = 1.622994712363500
B2 = 1.881168429118871
A2 = 170.546667227019526
B3 = 2.039533156416951
A3 = 65.739630248246584
D3 = 0.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 *a*' 481 (329)
ω_2 *a*' 424 (101)
ω_3 *a*' 350 (19)
ω_4 *a*' 268 (327)
ω_5 *a*' 78 (14)
ω_6 *a*'' 233 (2)

NaF_3 (C_{2v}, $^1A_1$): transition state

Coordinates of optimized geometry:

Na
F 1 B1
F 2 B2 1 A2
F 2 B2 1 A2 3 D3

B1 = 2.013331718504131
B2 = 1.765561299912435
A2 = 76.333929692915177
D3 = 180.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 a_1 462 (28)
ω_2 a_1 381 (0)
ω_3 a_1 193 (27)
ω_4 b_1 209 (4)
ω_5 b_2 568 (202)
ω_6 b_2 13*i* (3)

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

Coordinates of optimized geometry:

K
F 1 B1
F 2 B2 1 A2
F 2 B2 1 A2 3 D3

B1 = 2.307896606373894
B2 = 1.752415759745316
A2 = 79.578562394148832
D3 = 180.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 a_1 405 (12)
ω_2 a_1 373 (8)
ω_3 a_1 197 (34)
ω_4 b_1 224 (2)
ω_5 b_2 581 (257)
ω_6 b_2 66 (2)

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

Coordinates of optimized geometry:

Rb
F 1 B1
F 2 B2 1 A2
F 2 B2 1 A2 3 D3

B1 = 2.437070539899721
B2 = 1.749857742572373
A2 = 80.479054725695136
D3 = 180.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 a_1 398 (4)
ω_2 a_1 350 (6)
ω_3 a_1 175 (33)
ω_4 b_1 227 (1)
ω_5 b_2 583 (262)
ω_6 b_2 66 (3)

CsF_3 (C_{2v}, $^1A_1$): minimum

Coordinates of optimized geometry:

Cs
F 1 B1
F 2 B2 1 A2
F 2 B2 1 A2 3 D3

B1 = 2.588113836758844
B2 = 1.747714890956563
A2 = 81.559488676289149
D3 = 180.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 a_1 396 (3)
ω_2 a_1 333 (5)
ω_3 a_1 165 (36)
ω_4 b_1 231 (1)

ω_5 b_2 587 (255)
ω_6 b_2 63 (3)

CsF_3 (C_s, $^1A'$): minimum

Coordinates of optimized geometry:

Cs
F 1 B1
F 2 B2 1 A2
F 2 B3 1 A3 3 D3

B1 = 3.123421706185294
B2 = 2.246883223355252
A2 = 50.107247644301026
B3 = 1.455154196034556
A3 = 124.346838599510249
D3 = 180.000000000000000

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1 a' 748 (91)
ω_2 a' 330 (110)
ω_3 a' 178 (11)
ω_4 a' 127 (80)
ω_5 a' 44 (3)
ω_6 a'' 160 (2)

2. Optimized geometries and harmonic frequencies at the MRCISD+Q(4e,3o)/AVTZ level of theory

LiF_3 (C_{2v}, $^1A_1$): transition state

Coordinates of optimized geometry:

Li	0.0000000000	0.0000000000	-1.1834165306
F	0.0000000000	0.0000000000	0.5139248764
F	0.0000000000	1.6561404149	-0.0407838957
F	0.0000000000	-1.6561404149	-0.0407838957

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	713 (131)
ω_2	a_1	549 (2)
ω_3	a_1	196 (12)
ω_4	b_1	223 (0)
ω_5	b_2	706 (4)
ω_6	b_2	355*i* (3)

NaF_3 (C_{2v}, $^1A_1$): transition state

Coordinates of optimized geometry:

Na	0.0000000000	0.0000000000	-1.4850604688
F	0.0000000000	0.0000000000	0.8040477503
F	0.0000000000	1.7559369822	0.4965084256
F	0.0000000000	-1.7559369822	0.4965084256

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	846 (34)
ω_2	a_1	384 (18)
ω_3	a_1	196 (14)
ω_4	b_1	204 (0)
ω_5	b_2	689 (0)
ω_6	b_2	88*i* (13)

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

Coordinates of optimized geometry:

K	0.0000000000	0.0000000000	-1.2201346498
F	0.0000000000	0.0000000000	1.0601539788
F	0.0000000000	1.6992570846	0.7254282912
F	0.0000000000	-1.6992570846	0.7254282912

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	488 (9)
ω_2	a_1	403 (20)
ω_3	a_1	210 (29)
ω_4	b_1	231 (0)
ω_5	b_2	602 (10)
ω_6	b_2	69 (23)

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

Coordinates of optimized geometry:

Rb	0.0000000000	0.0000000000	-0.8859025700
F	0.0000000000	0.0000000000	1.5306118596
F	0.0000000000	1.7039946530	1.2273916584
F	0.0000000000	-1.7039946530	1.2273916584

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	481 (5)
ω_2	a_1	369 (11)
ω_3	a_1	188 (30)
ω_4	b_1	234 (0)
ω_5	b_2	590 (15)
ω_6	b_2	105 (26)

CsF_3 (C_{2v}, $^1A_1$): minimum

Coordinates of optimized geometry:

Cs	0.0000000000	0.0000000000	-0.7235432115
F	0.0000000000	0.0000000000	1.8583396873

F	0.0000000000	1.7082596726	1.6016428761
F	0.0000000000	-1.7082596726	1.6016428761

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	478 (3)
ω_2	a_1	347 (9)
ω_3	a_1	173 (35)
ω_4	b_1	240 (0)
ω_5	b_2	588 (20)
ω_6	b_2	104 (24)

3. Optimized geometries and harmonic frequencies at the CASPT2(4e,3o)/AVTZ level of theory

LiF_3 (C_{2v}, $^1A_1$): transition state

Coordinates of optimized geometry:

Li	0.0000000000	0.0000000000	-1.1886666724
F	0.0000000000	0.0000000000	0.5384993718
F	0.0000000000	1.6487474878	-0.0521120830
F	0.0000000000	-1.6487474878	-0.0521120830

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	695 (0)
ω_2	a_1	656 (148)
ω_3	a_1	196 (33)
ω_4	b_1	221 (40)
ω_5	b_2	712 (282)
ω_6	b_2	386*i* (705)

NaF_3 (C_{2v}, $^1A_1$): transition state

Coordinates of optimized geometry:

Na	0.0000000000	0.0000000000	-1.4729429298
F	0.0000000000	0.0000000000	0.8258265084
F	0.0000000000	1.7545236772	0.4782873584
F	0.0000000000	-1.7545236772	0.4782873584

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	879 (1318)
ω_2	a_1	428 (310)
ω_3	a_1	195 (52)
ω_4	b_1	198 (3)
ω_5	b_2	679 (457)
ω_6	b_2	117*i* (20)

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

Coordinates of optimized geometry:

K	0.0000000000	0.0000000000	-1.2123995093
F	0.0000000000	0.0000000000	1.0704270776
F	0.0000000000	1.7115314919	0.7123323663
F	0.0000000000	-1.7115314919	0.7123323663

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	538 (0)
ω_2	a_1	394 (21)
ω_3	a_1	208 (35)
ω_4	b_1	217 (2)
ω_5	b_2	623 (1629)
ω_6	b_2	95 (0)

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

Coordinates of optimized geometry:

Rb	0.0000000000	0.0000000000	-0.8798399369
F	0.0000000000	0.0000000000	1.5365168271
F	0.0000000000	1.7175310472	1.2108022411
F	0.0000000000	-1.7175310472	1.2108022411

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	529 (0)
ω_2	a_1	359 (10)
ω_3	a_1	188 (34)
ω_4	b_1	220 (1)
ω_5	b_2	612 (1545)
ω_6	b_2	118 (4)

CsF_3 (C_{2v}, $^1A_1$): minimum

Coordinates of optimized geometry:

Cs	0.0000000000	0.0000000000	-0.7167370682

F	0.0000000000	0.0000000000	1.8575417801
F	0.0000000000	1.7230407308	1.5782352711
F	0.0000000000	-1.7230407308	1.5782352711

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	526 (0)
ω_2	a_1	338 (8)
ω_3	a_1	174 (38)
ω_4	b_1	225 (1)
ω_5	b_2	611 (1348)
ω_6	b_2	114 (8)

4. Multireference Diagnostic (C_0, C_1, and C_2 coefficients) at the CASSCF(16e,10o)/AVTZ level of theory

Species	C_0	C_1	C_2	C_0^2	C_1^2	C_2^2
LiF_3 (C_s, $^1A'$)	0.964116	0.2430709	−	0.93	0.06	−
LiF_3 (C_{2v}, $^1A_1$)	0.873829	0.4568559	0.113757	0.76	0.21	0.01
NaF_3 (C_s, $^1A'$, loose type)	0.951928	0.2903616	0.075057	0.91	0.08	0.01
NaF_3 (C_s, $^1A'$, tight type)	0.934912	0.3376876	0.051117	0.87	0.11	0.00
NaF_3 (C_{2v}, $^1A_1$)	0.911969	0.3683825	0.132125	0.83	0.14	0.02
KF_3 (C_{2v}, $^1A_1$)	0.911490	0.3704887	0.131562	0.83	0.14	0.02
RbF_3 (C_{2v}, $^1A_1$)	0.921691	0.3377843	0.142495	0.85	0.11	0.02
CsF_3 (C_{2v}, $^1A_1$)	0.922366	0.3362211	0.141855	0.85	0.11	0.02
CsF_3 (C_s, $^1A'$)	0.961448	0.2547246	−	0.92	0.06	−

5. Optimized geometries and harmonic frequencies of the C_{2v} CsF_3 at various levels of theory

- CCSD(T)/AVTZ:

Coordinates of optimized geometry:

Cs	-0.000000	0.000000	0.717615
F	-0.000000	0.000000	-1.854606
F	-0.000000	1.726153	-1.582775
F	0.000000	-1.726153	-1.582775

Harmonic vibrational frequencies (cm^{-1}), symmetries, and intensities (in parentheses, km mol^{-1}):

ω_1	a_1	398 (4)
ω_2	a_1	341 (7)
ω_3	a_1	171 (35)
ω_4	b_1	227 (1)
ω_5	b_2	622 (270)
ω_6	b_2	70 (4)

- CCSDT/AVTZ:

Coordinates of optimized geometry:

Cs	0.0000000000	0.0000000000	-0.7190876366
F	0.0000000000	0.0000000000	1.8551419686
F	-0.0000000000	1.7201515486	1.5876579586
F	0.0000000000	-1.7201515486	1.5876579586

Harmonic vibrational frequencies (cm^{-1}) and symmetries:

ω_1	a_1	415
ω_2	a_1	342
ω_3	a_1	172
ω_4	b_1	229
ω_5	b_2	605
ω_6	b_2	64

- CCSDT(Q)/AVTZ:

Coordinates of optimized geometry:

Cs	0.0000000000	0.0000000000	-0.7156715860
F	0.0000000000	0.0000000000	1.8573904620
F	-0.0000000000	1.7364598360	1.5745850301
F	0.0000000000	-1.7364598360	1.5745850301

Harmonic vibrational frequencies (cm^{-1}) and symmetries:

ω_1	a_1	385
ω_2	a_1	332
ω_3	a_1	169
ω_4	b_1	214
ω_5	b_2	572
ω_6	b_2	74

- CASPT2(4e,3o)/AVTZ:

Coordinates of optimized geometry:

Cs	0.0000000000	0.0000000000	-0.7167370682
F	0.0000000000	0.0000000000	1.8575417801
F	0.0000000000	1.7230407308	1.5782352711
F	0.0000000000	-1.7230407308	1.5782352711

Harmonic vibrational frequencies (cm^{-1}) and symmetries:

ω_1	a_1	526
ω_2	a_1	338
ω_3	a_1	174
ω_4	b_1	225
ω_5	b_2	611
ω_6	b_2	114

- CASPT3(4e,3o)/AVTZ:

Coordinates of optimized geometry:

Cs	0.0000000000	0.0000000000	-0.7251856839
F	0.0000000000	0.0000000000	1.8604005595
F	0.0000000000	1.6939907824	1.6063574878
F	0.0000000000	-1.6939907824	1.6063574878

Harmonic vibrational frequencies (cm^{-1}) and symmetries:

ω_1	a_1	515
ω_2	a_1	354
ω_3	a_1	176
ω_4	b_1	251
ω_5	b_2	521
ω_6	b_2	115

- MRCISD+Q(4e,3o)/AVTZ:

Coordinates of optimized geometry:

Cs	0.0000000000	0.0000000000	-0.7235432115
F	0.0000000000	0.0000000000	1.8583396873
F	0.0000000000	1.7082596726	1.6016428761
F	0.0000000000	-1.7082596726	1.6016428761

Harmonic vibrational frequencies (cm^{-1}) and symmetries:

ω_1	a_1	478
ω_2	a_1	347
ω_3	a_1	173
ω_4	b_1	240
ω_5	b_2	588
ω_6	b_2	104