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**Electronic Supporting Information (ESI)**

# Effect of alkali ions on optical properties of flavins: Vibronic spectra of cryogenic $M^+$lumiflavin complexes (M=Li-Cs)

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**Figure S1.** Photodissociation mass spectra of $Na^+LF$ with laser off and on (resonant to $S_1$ origin at 18310 $cm^{-1}$). The photodissociation efficiency is around 2%.

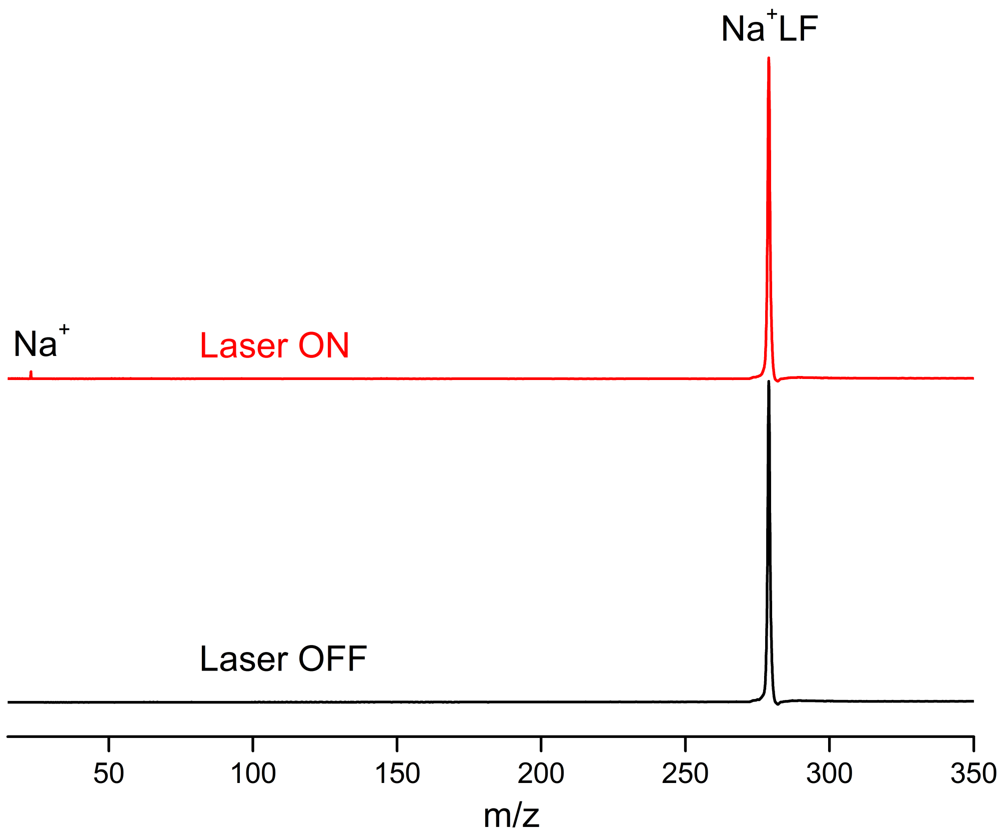
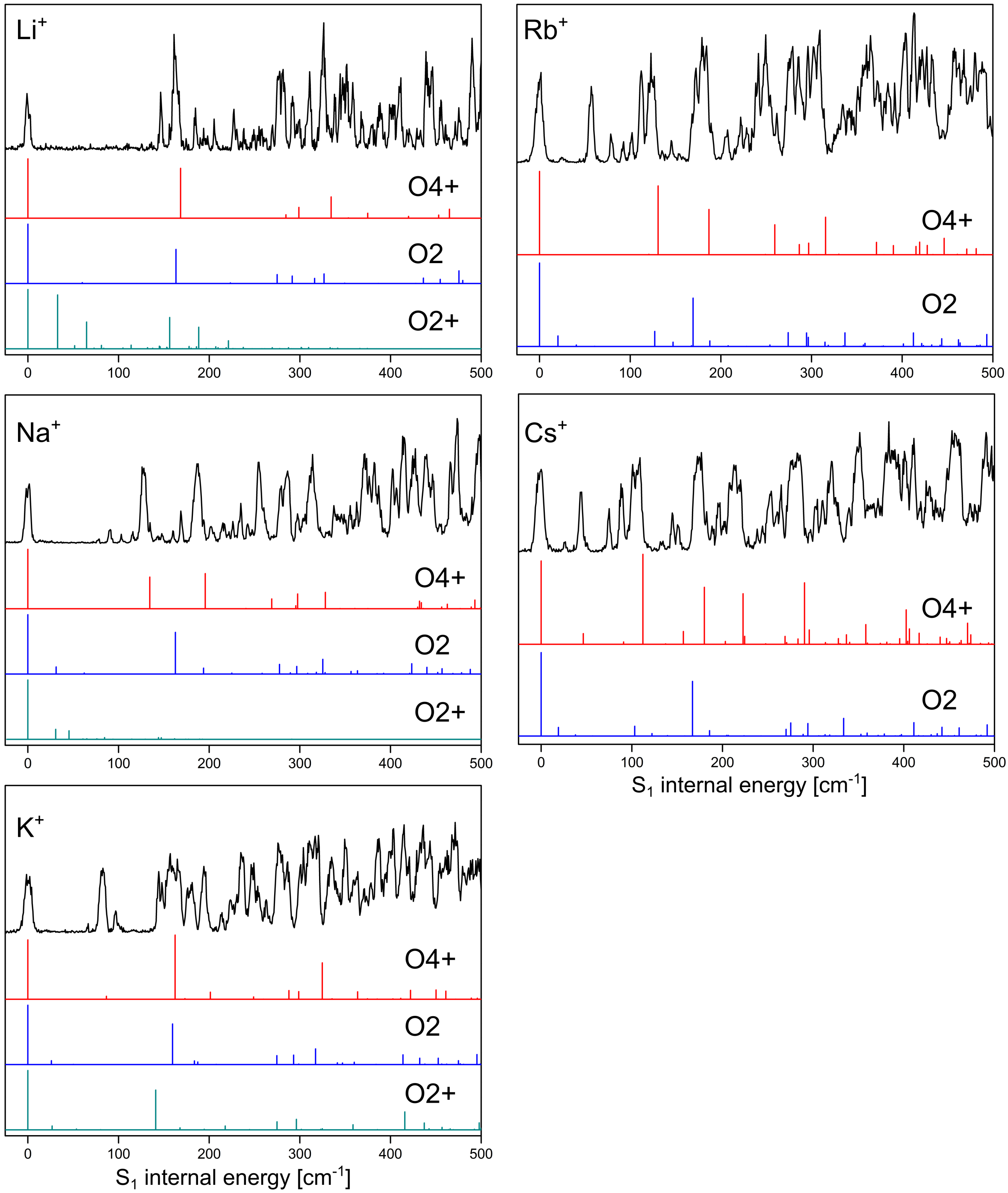


**Figure S2.** Comparison between measured VISPD spectra of $M^+LF$ with M=(Li-Cs) and Franck-Condon (FC) simulations for the three most stable isomers shown in Figure 1 as a function of $S_1$ internal energy. Clearly, the FC simulations of the O4+ isomer fits best, in particular when comparing the main (i.e., intense) transitions.



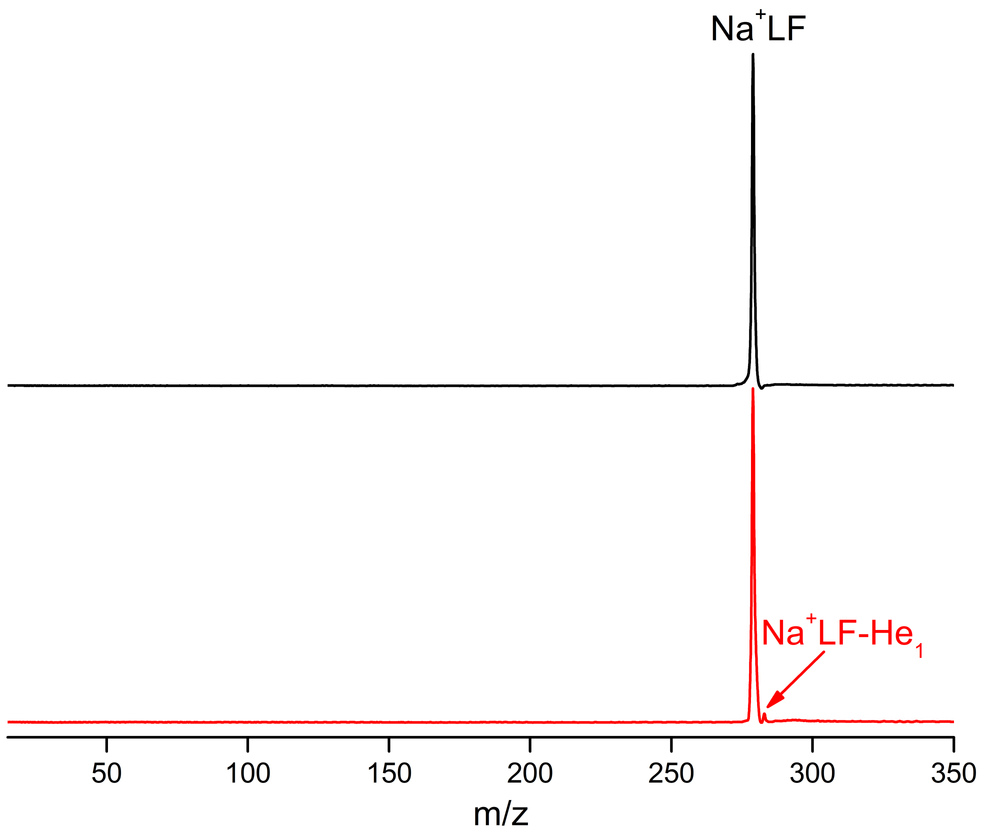



**Figure S3.** Laser-off mass spectra of trapping mass-selected $Na^+LF$ ions measured at trap temperatures of 13 K (black) and 6 K (red). At T=6 K, He-tagged complexes of the type $Na^+LF$-He are observed (2% of $Na^+LF$). At T=13 K, no such complexes are formed in the cryogenic 22-pole trap.

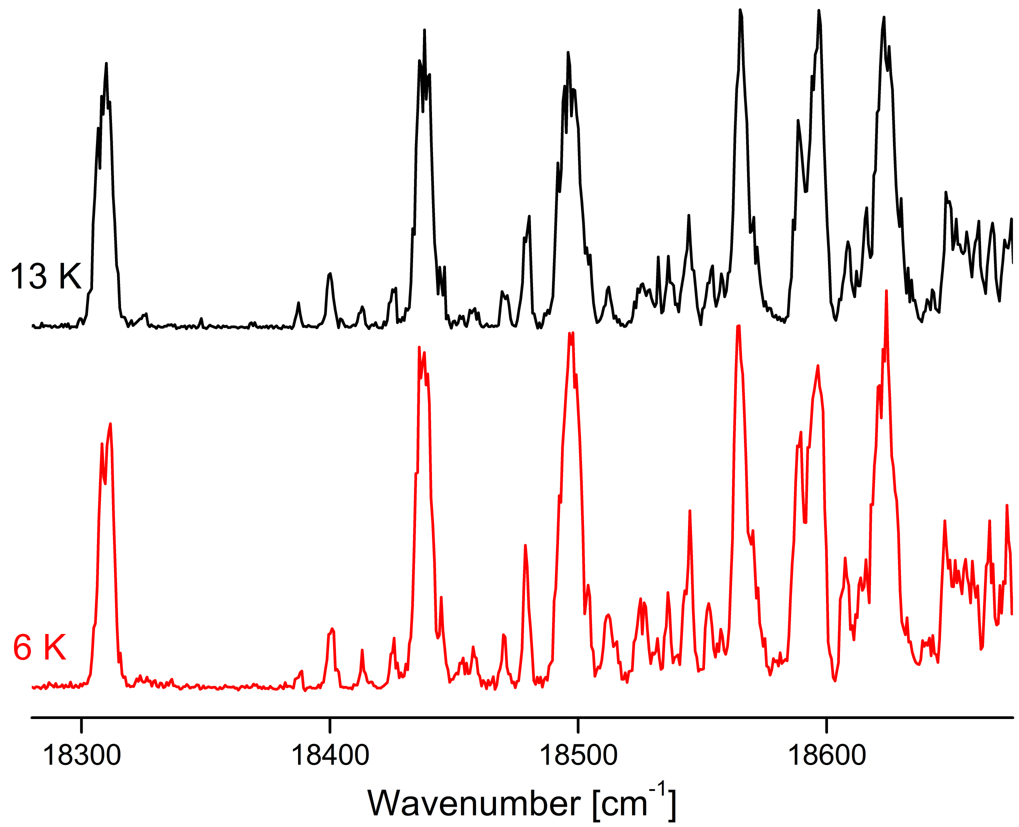
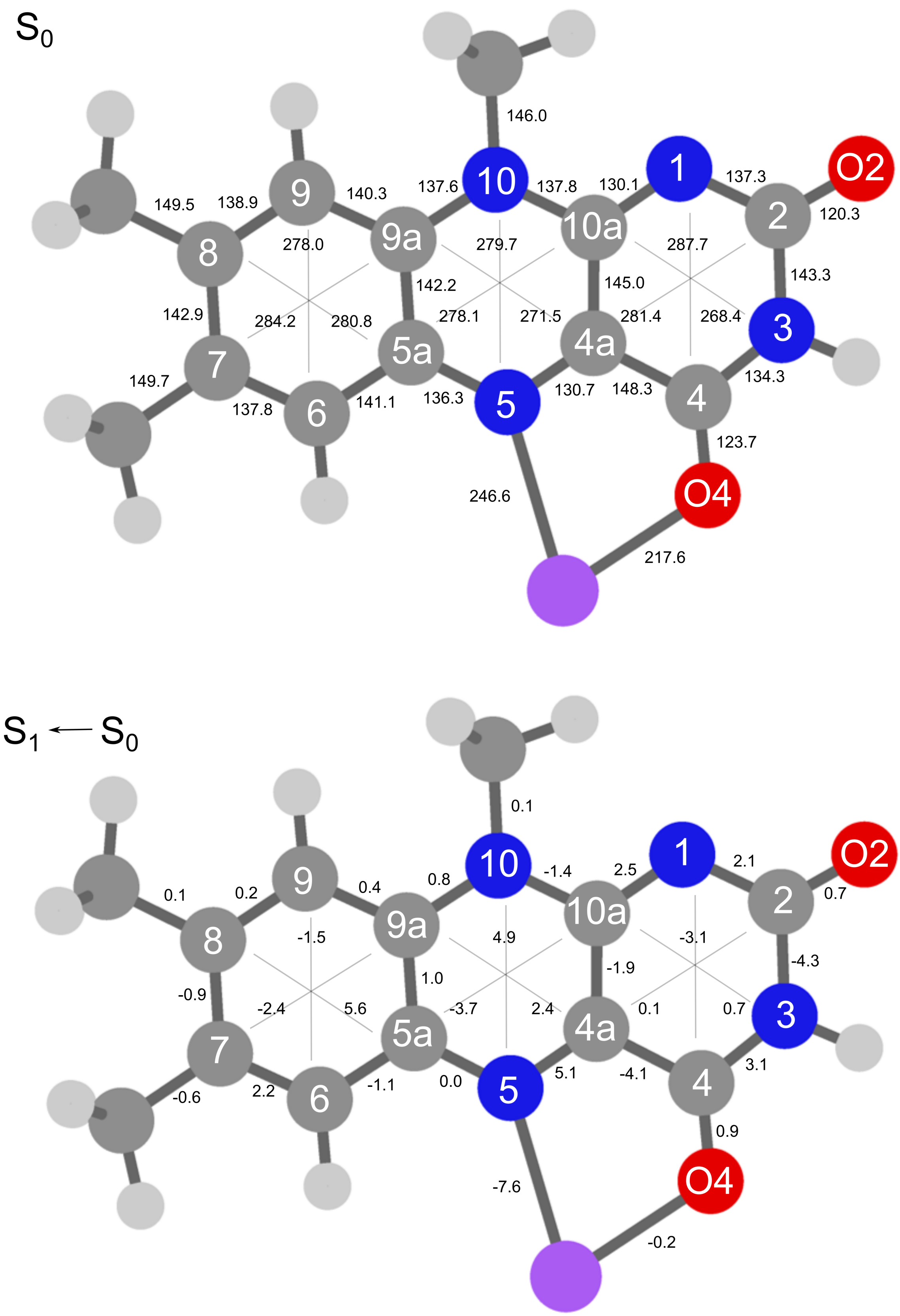



**Figure S4.** VISPD spectra of $Na^+LF$ after mass-selection, trapping, and cooling at trap temperatures of T=13 K (black, no He adducts formed) and at T=6 K (red, He adducts formed). The spectra are very similar indicating that the contribution of the He adducts to the VISPD spectrum at 6 K is negligible.

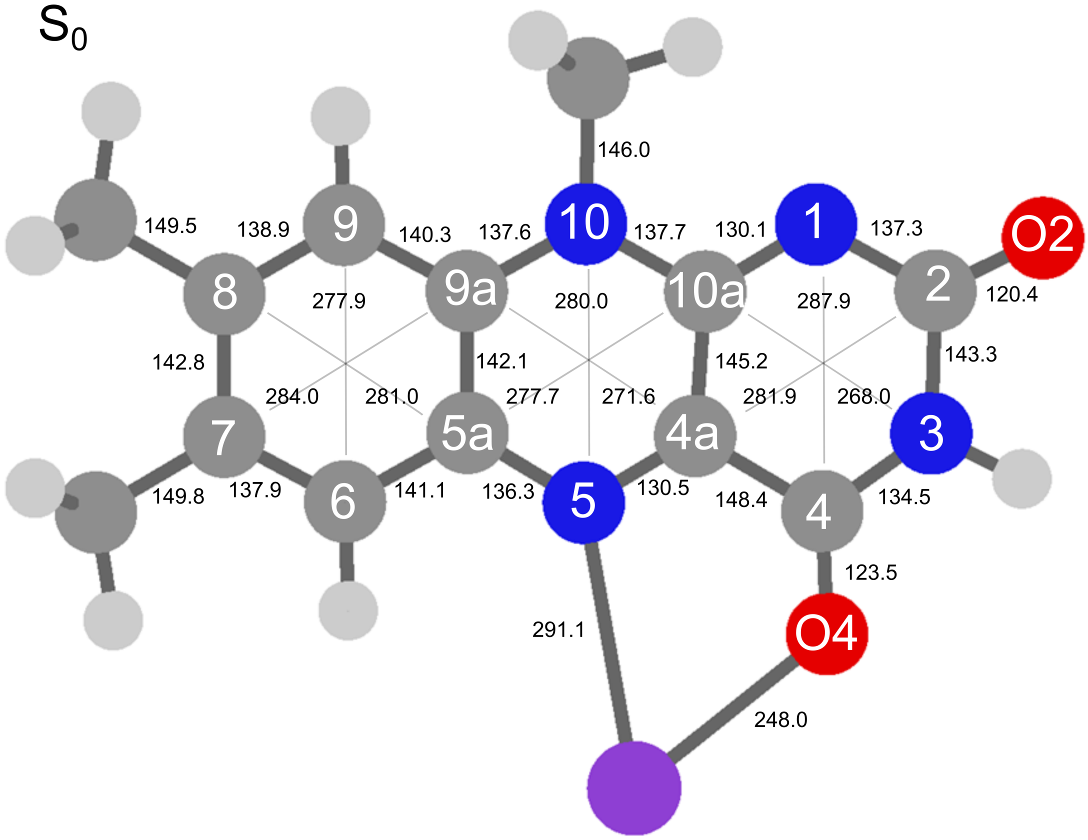
**Figure S5.** (Top) Absolute distances (in pm) of $M^{+}LF$ (M=Na-Cs) and LF in its $S_0$ state calculated at the PBE0/cc-pVDZ level. (Bottom) Relative changes in bond distances upon electronic $S_1$ excitation. Positive (negative) values indicate elongations (contractions).

**$Na^{+}LF$**

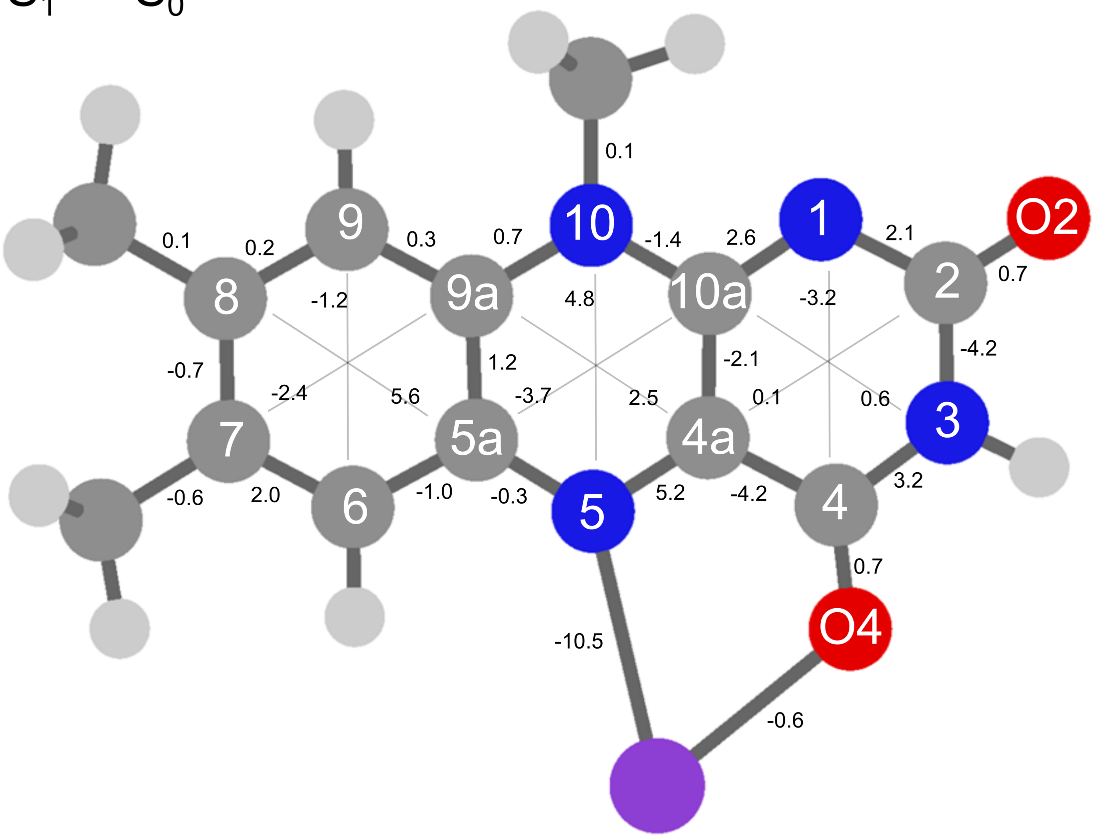


**$K^+LF$**

$S_0$

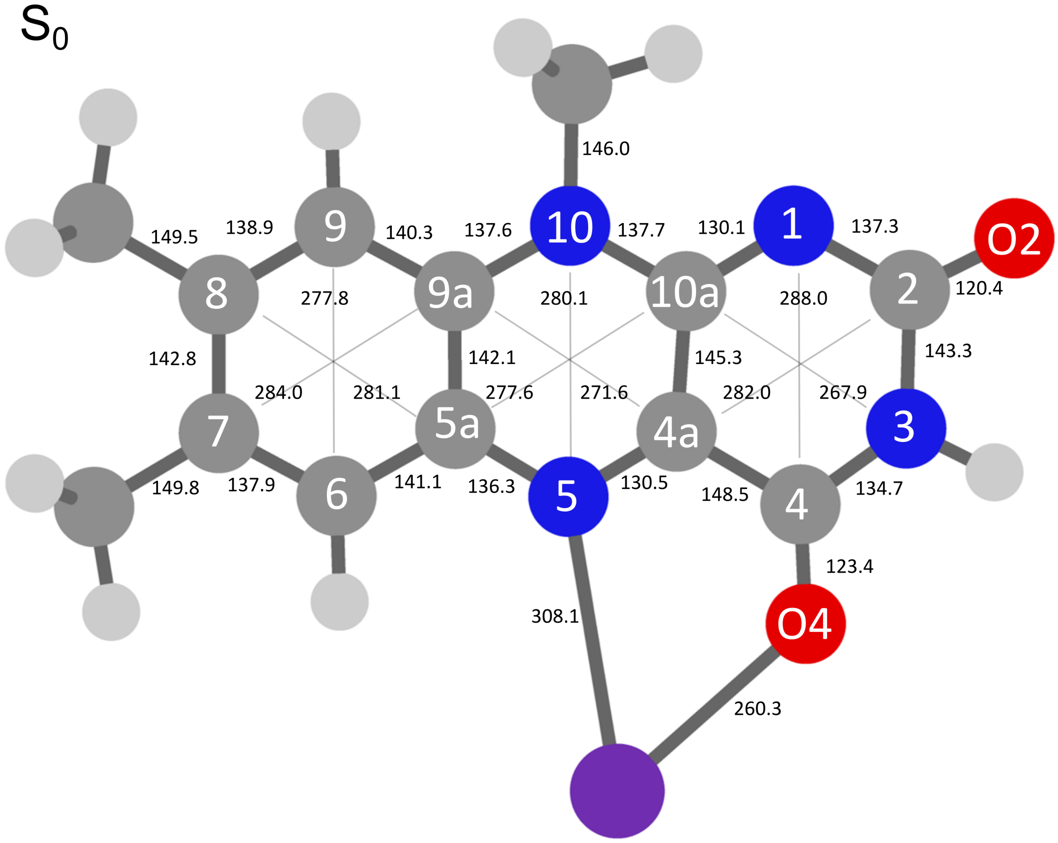



$S_1 \leftarrow S_0$

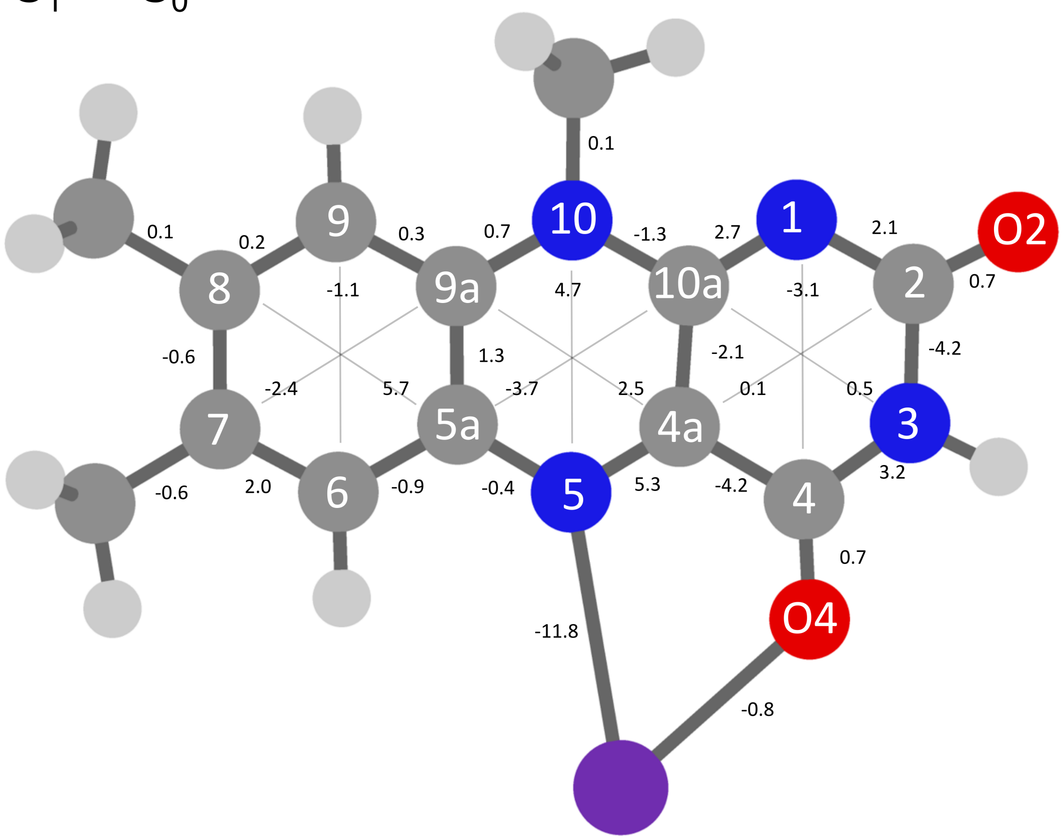


**Rb$^+$LF**

$S_0$

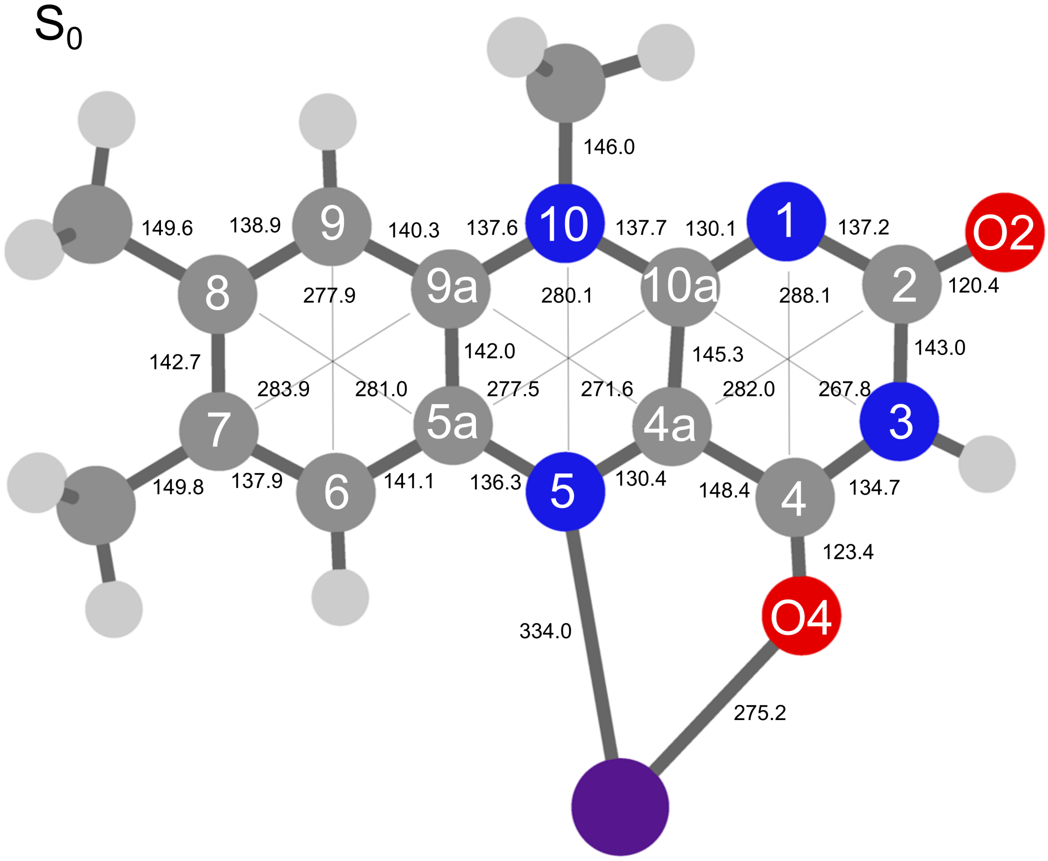



$S_1 \leftarrow S_0$

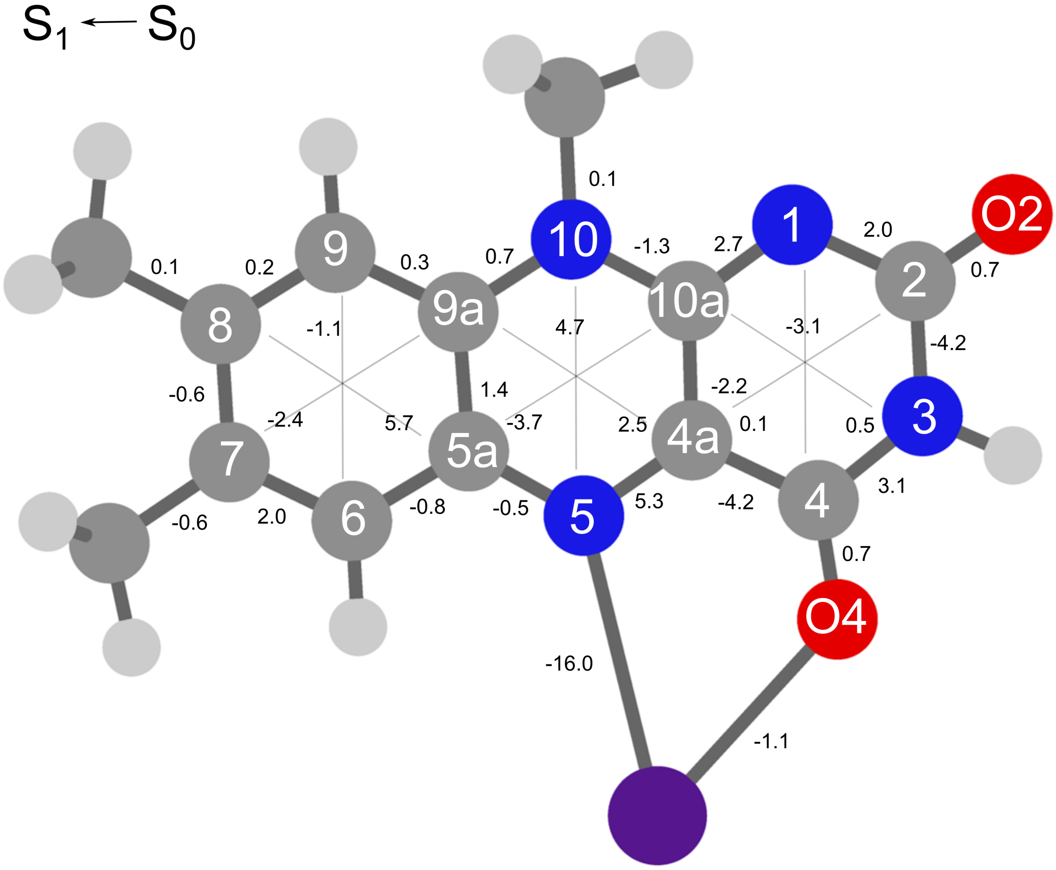


**$Cs^{+}LF$**

$S_0$

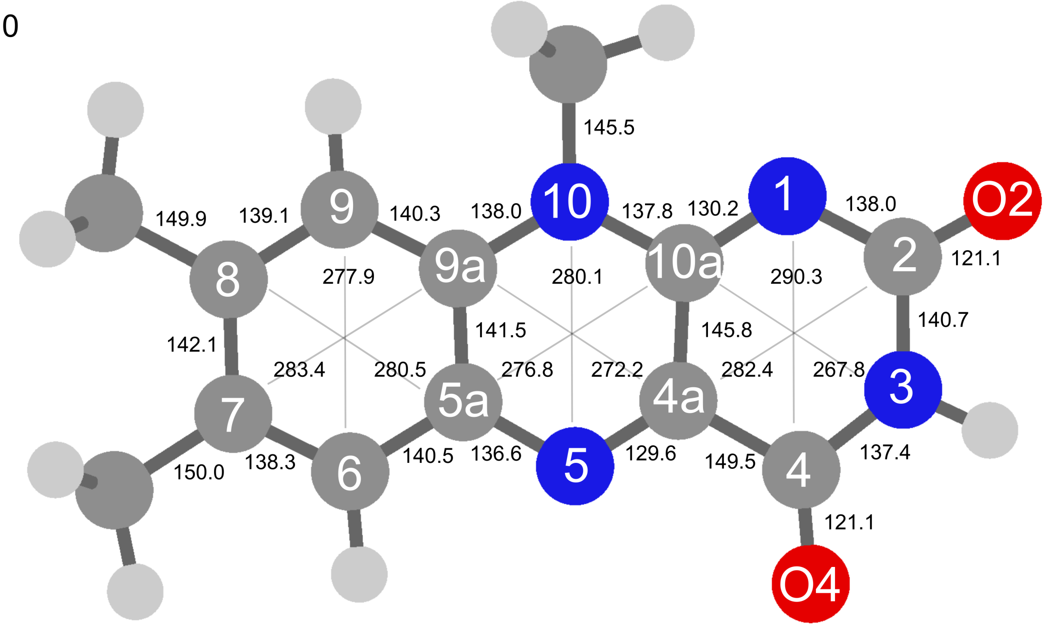



$S_1 \leftarrow S_0$



**LF**

$S_0$




$S_1 \leftarrow S_0$

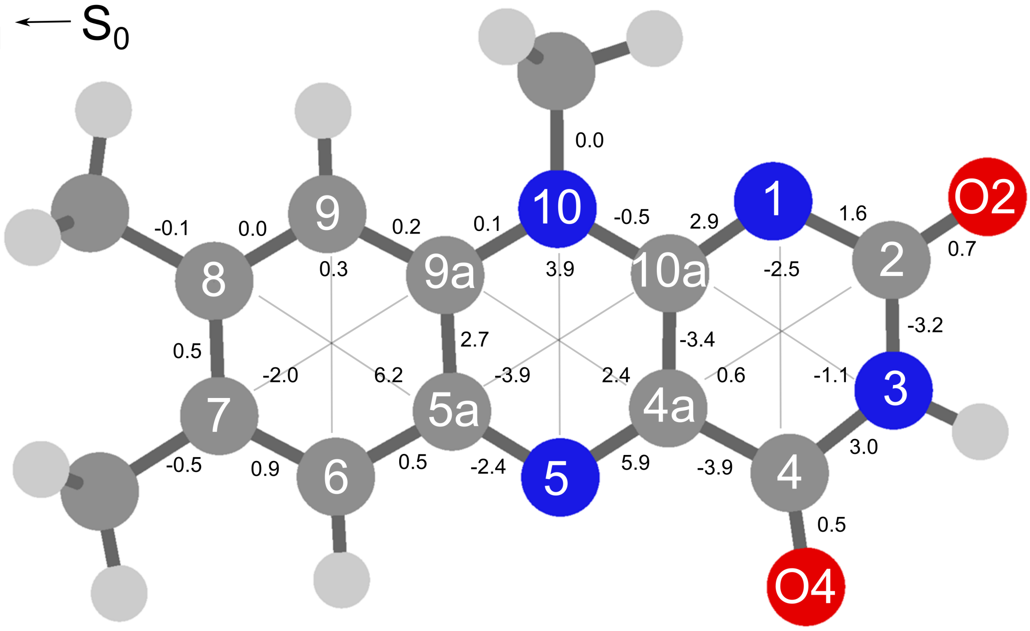


**Figure S6.** Dependence of the $S_1$ origin intensities of $M^+LF$ with M=Li-Cs on the laser pulse energy compared to a fit to a polynom with degree n=1 (linear, M=Na-Cs) and n=1-3 (linear, quadratic, cubic; M=Li). While for M=Na-Cs, the linear fit reproduces the experimental data points well, for Li clearly a quadratic (blue) to cubic (pink) function fits much better.

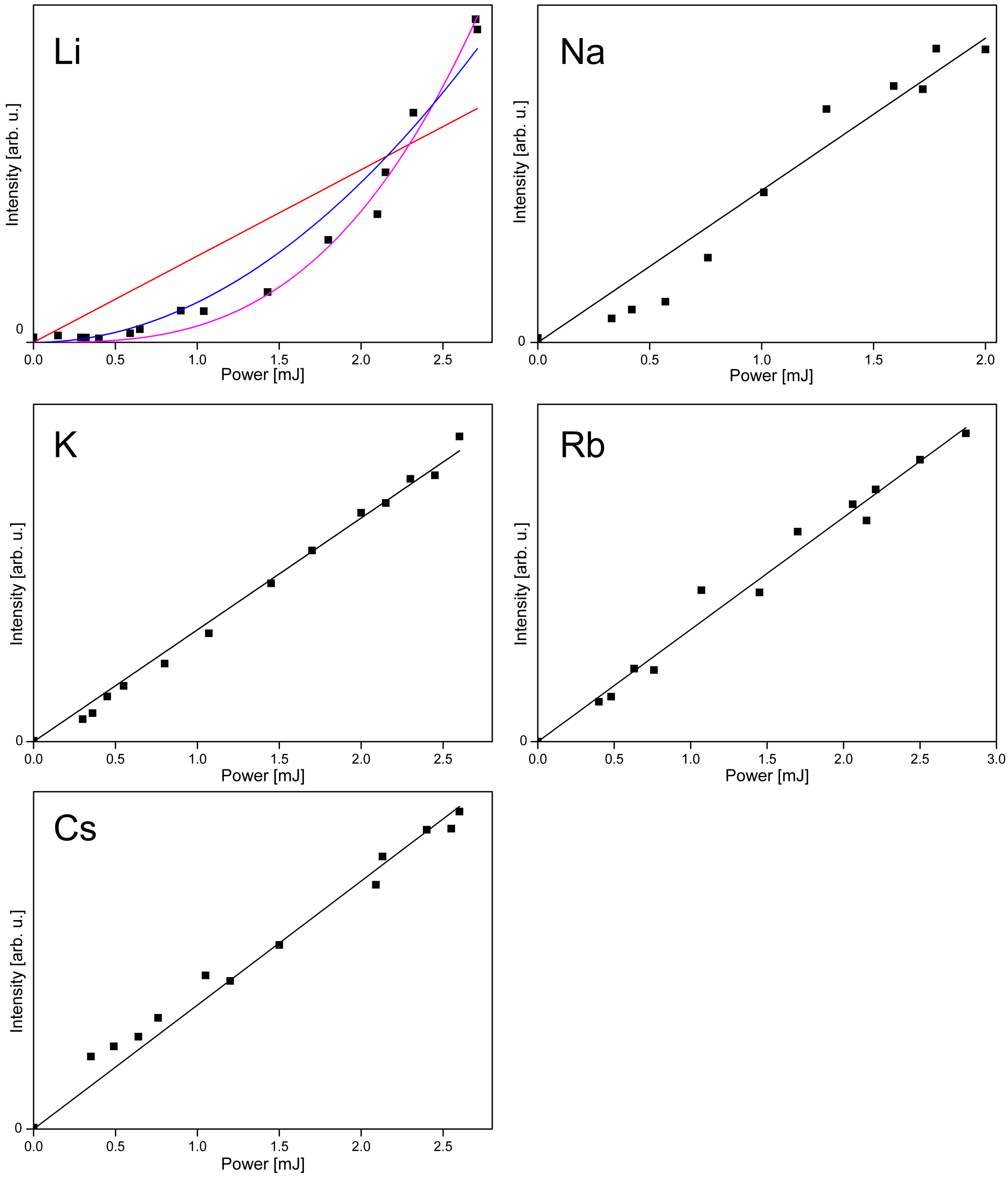


**Table S1.** Experimental frequencies for vibronic transitions (in $cm^{-1}$) observed in the VISPD spectra of the $S_1$ states of $M^+LF$ (M=Li-Cs) compared to harmonic frequencies of the $M^+LF(O4+)$ isomers computed at the PBE0/cc-pVDZ level, along with the mode assignment. The normal modes σ, β, and m1 etc. are similar to those of $M^+LC(O4+)$ discussed in Nieto et al. PCCP **20**, 22148 (2018). The m4* mode is special to the LF chromophore and corresponds to the in-plane bend of the $CH_3$ group at N10.

## $Li^+LF$

| | ν (exp) | ν (calc) | Assignment |
|---|---|---|---|
| | 17645 | 18022 | $0^0$ |
| A | 163 | 167 | m1 |
| B | 281 | 284 | m2 |
| C | 292 | 297 | m3 |
| D | 311 | 318 | m4 |
| E | 326 | 334 | 2m1 |
| F | 368 | 375 | β |
| G | 410 | 419 | m5 |
| H | 440 | 447 | m6 |
| I | 446 | 451 | m1+m2 |
| J | 456 | 464 | m1+m3 |
| K | 477 | 485 | m1+m4 |
| L | 490 | 501<br>501 | 3m1<br>m7 |
| M | 503 | 515 | m8 |
| N | 533 | 542 | β+m1 |

**$Na^{+}LF$**

| | ν (exp) | ν (calc) | Assignment |
|---|---|---|---|
| | 18310 | 18784 | $0^0$ |
| A | 128 | 134 | β |
| B | 187 | 194 | m1 |
| C | 234 | 240 | σ |
| D | 256 | 268 | 2β |
| E | 279 | 295 | m2 |
| F | 286 | 298 | m3 |
| G | 313 | 328 | m1+β |
| H | 338 | 343 | m4 |
| I | 355 | 361 | m4* |
| J | 363 | 374 | σ+β |
| K | 371 | 388 | 2m1 |
| L | 382 | 402 | 3β |
| M | 407 | 429 | m2+β |
| N | 414 | 432 | m3+β |
| O | 426 | 434<br>433 | m1+σ<br>m6 |
| P | 439 | 462 | m1+2β |
| Q | 447 | 455 | m5 |
| R | 465 | 489 | m1+m2 |
| S | 473 | 492 | m1+m3 |
| T | 497 | 498 | m7 |

**$K^+LF$**

| | ν (exp) | ν (calc) | Assignment |
|---|---|---|---|
| | 18778 | 19279 | $0^0$ |
| A | 82 | 86 | β |
| B | 157 | 162 | σ |
| C | 164 | 172 | 2β |
| D | 194 | 202 | m1 |
| E | 236 | 248 | σ+β |
| F | 247 | 258 | 3β |
| G | 278 | 288 | m1+β |
| H | 286 | 287 | m2 |
| I | 302 | 295 | m3 |
| J | 311 | 324 | 2σ |
| K | 318 | 334 | σ+2β |
| L | 335 | 332 | m4 |
| M | 350 | 364 | m1+σ |
| N | 360 | 360 | m4* |
| O | 371 | 373 | m2+β |
| P | 378 | 381 | m3+β |
| Q | 386 | 404 | 2m1 |
| R | 401 | 420 | 3β+σ |
| S | 415<br>415 | 418<br>421 | m4+β<br>m6 |
| T | 435 | 449 | m2+σ |
| U | 443 | 450<br>457 | m5<br>m3+σ |

**$Rb^+LF$**

| | ν (exp) | ν (calc) | Assignment |
|---|---|---|---|
| | 18914 | 19451 | $0^0$ |
| A | 57 | 60 | β |
| B | 112 | 120 | 2β |
| C | 124 | 130 | σ |
| D | 172 | 180 | 3β |
| E | 179 | 190 | β+σ |
| F | 184 | 185 | m1 |
| G | 240 | 245 | m1+β |
| H | 249 | 260 | 2σ |
| I | 285 | 285 | m2 |
| J | 296 | 296 | m3 |
| K | 303 | 315 | m1+σ |
| L | 308 | 320 | 2σ+β |
| M | 335 | 330 | m4 |
| N | 361 | 360 | m4* |
| O | 366 | 370 | 2m1 |
| P | 402 | 415 | m2+σ |
| Q | 413 | 419 | m6 |
| R | 422 | 426 | m3+σ |
| S | 457<br>458 | 460<br>450 | m4+σ<br>m5 |
| T | 468 | 470 | m1+m2 |
| U | 480 | 481 | m1+m3 |
| V | 489 | 495 | m7 |

**$Cs^+LF$**

| | ν (exp) | ν (calc) | Assignment |
|---|---|---|---|
| | 19031 | 19658 | $0^0$ |
| A | 44 | 45 | β |
| B | 88 | 90 | 2β |
| C | 108 | 111 | σ |
| D | 148 | 156 | β+σ |
| E | 175 | 179 | m1 |
| F | 196 | 201 | 2β+σ |
| G | 214 | 222<br>224 | 2σ<br>m1+β |
| H | 254 | 267 | 2σ+β |
| I | 264 | 269 | 2β+m1 |
| J | 276<br>284<br>280 | 283<br>294<br>290 | m2<br>m3<br>m1+σ |
| K | 299 | 312 | 2β+2σ |
| L | 311 | 314 | 3β+m1 |
| M | 320 | 328 | m4 |
| N | 350 | 360<br>358 | m4*<br>2m1 |
| O | 387 | 401 | 2σ+m1 |
| P | 401 | 416 | m5 |
| Q | 410 | 449 | m6 |
| R | 427 | 439 | m4+σ |
| S | 457 | 462<br>473 | m1+m2<br>m1+m3 |
| T | 493 | 505<br>516 | 2σ+m2<br>2σ+m3 |

**Table S2.** Low-energy intramolecular in-plane vibrational frequencies (in $cm^{-1}$) in the $S_1$ state of LF and $M^+LF(O4+)$ with M=Li-Cs calculated at the PBE0/cc-pVDZ level compared to experimental data.

| | Li | | Na | | K | | Rb | | Cs | | LF | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mode | $S_1$ | exp | $S_1$ | exp | $S_1$ | exp | $S_1$ | exp | $S_1$ | exp | $S_1$ | exp[a] |
| m1 | 167 | 163 | 194 | 187 | 202 | 194 | 185 | 184 | 179 | 175 | 165 | 164 |
| m2 | 284 | 281 | 295 | 279 | 287 | 286 | 285 | 285 | 283 | 276 | 276 | 274 |
| m3 | 297 | 292 | 298 | 286 | 295 | 302 | 296 | 296 | 294 | 284 | 294 | |
| m4 | 318 | 311 | 343 | 338 | 332 | 335 | 330 | 335 | 328 | 320 | 322 | |
| m4* | 352 | ? | 361 | 355 | 360 | 360 | 360 | 361 | 360 | 350 | 358 | |
| m5 | 419 | 410 | 455 | 447 | 450 | 443 | 450 | 458 | 416 | 401 | 409 | 403 |
| m6 | 447 | 440 | 433 | 426 | 421 | 415 | 419 | 413 | 449 | 410 | 444 | 440 |
| m7 | 501 | 490 | 498 | 497 | 495 | | 495 | 489 | 494 | | 489 | |
| m8 | 515 | 503 | 532 | | 529 | | 528 | | 527 | | 521 | 513 |
| m9 | 550 | | 550 | | 549 | | 548 | | 548 | | 545 | |
| m10 | 577 | | 615 | | 613 | | 613 | | 612 | | 603 | 593 |

[a] Values from He droplet spectrum (Vdovin et al., Chem. Phys. **422**, 195 (2013)).

**Table S3.** Harmonic vibrational frequencies ($cm^{-1}$) of LF and $M^{+}$LF(O4+) with M=Li-Cs in the $S_0$ and $S_1$ states (Mulliken notation) calculated at the PBE0/cc-pVDZ level.

## $Li^{+}$LF

| $S_0$ | | $S_1$ | |
|---|---|---|---|
| a" | a' | a" | a' |
| 46.85 | 164.09 | 45.80 | 166.92 |
| 64.48 | 285.88 | 57.73 | 283.96 |
| 101.47 | 298.62 | 90.87 | 297.11 |
| 120.86 | 320.32 | 112.89 | 317.69 |
| 135.00 | 335.66 | 119.11 | 351.67 |
| 161.78 | 362.05 | 147.99 | 374.52 |
| 176.86 | 410.92 | 169.39 | 419.09 |
| 190.42 | 444.09 | 198.42 | 446.95 |
| 194.68 | 500.34 | 200.01 | 500.61 |
| 215.65 | 509.69 | 217.53 | 515.39 |
| 252.45 | 556.19 | 232.78 | 549.96 |
| 340.73 | 582.01 | 338.71 | 577.23 |
| 383.39 | 617.92 | 357.70 | 625.65 |
| 459.44 | 646.66 | 416.33 | 639.86 |
| 537.63 | 697.44 | 492.65 | 691.88 |
| 638.62 | 760.18 | 621.71 | 746.80 |
| 679.01 | 798.10 | 645.33 | 795.03 |
| 752.12 | 855.69 | 680.04 | 845.84 |
| 769.85 | 886.93 | 731.71 | 888.00 |
| 791.25 | 997.73 | 759.06 | 997.64 |
| 829.29 | 1013.00 | 776.78 | 1013.32 |
| 873.94 | 1027.44 | 876.62 | 1021.82 |
| 884.24 | 1036.67 | 885.79 | 1032.01 |
| 1027.15 | 1107.54 | 1012.24 | 1101.12 |
| 1052.28 | 1179.32 | 1043.14 | 1176.54 |
| 1132.73 | 1211.87 | 1128.75 | 1192.69 |
| 1438.96 | 1221.30 | 1432.09 | 1224.94 |
| 1454.57 | 1267.25 | 1450.63 | 1250.94 |
| 1476.59 | 1278.79 | 1467.44 | 1276.38 |
| 3134.01 | 1343.95 | 3118.36 | 1300.80 |
| 3138.19 | 1363.63 | 3131.67 | 1342.36 |
| 3175.52 | 1376.22 | 3172.87 | 1363.82 |
| | 1388.08 | | 1376.96 |
| | 1396.39 | | 1387.87 |
| | 1402.34 | | 1393.48 |
| | 1423.46 | | 1406.25 |
| | 1436.04 | | 1414.53 |
| | 1452.02 | | 1418.02 |
| | 1463.86 | | 1441.58 |
| | 1490.98 | | 1457.05 |
| | 1495.85 | | 1468.45 |
| | 1524.91 | | 1488.39 |
| | 1548.71 | | 1522.23 |
| | 1594.36 | | 1531.60 |
| | 1630.44 | | 1563.26 |
| | 1667.54 | | 1610.16 |
| | 1709.16 | | 1675.88 |
| | 1769.57 | | 1716.74 |
| | 1870.70 | | 1783.13 |
| | 3061.91 | | 3051.13 |
| | 3063.68 | | 3059.58 |
| | 3080.78 | | 3080.45 |
| | 3173.74 | | 3175.03 |
| | 3181.08 | | 3179.01 |
| | 3204.75 | | 3212.94 |
| | 3221.60 | | 3230.14 |
| | 3252.45 | | 3247.13 |
| | 3584.82 | | 3614.12 |

## $Na^+LF$

| $S_0$ a'' | a' | $S_1$ a'' | a' |
|---|---|---|---|
| 40.66 | 121.09 | 41.18 | 133.81 |
| 62.83 | 180.67 | 54.05 | 194.08 |
| 71.99 | 240.50 | 62.86 | 240.31 |
| 101.53 | 296.25 | 99.92 | 294.68 |
| 134.75 | 300.06 | 118.95 | 297.53 |
| 146.50 | 346.49 | 121.54 | 343.05 |
| 165.62 | 357.71 | 158.87 | 360.71 |
| 175.42 | 425.82 | 176.81 | 432.95 |
| 193.12 | 452.63 | 193.81 | 454.74 |
| 211.54 | 505.12 | 217.30 | 497.95 |
| 252.78 | 528.12 | 233.06 | 531.67 |
| 339.89 | 553.90 | 338.13 | 550.14 |
| 381.65 | 609.82 | 351.41 | 615.07 |
| 458.18 | 644.18 | 415.97 | 637.05 |
| 532.04 | 686.17 | 490.23 | 677.91 |
| 638.58 | 761.41 | 621.77 | 746.62 |
| 678.75 | 795.26 | 647.13 | 790.41 |
| 750.87 | 850.00 | 680.85 | 838.44 |
| 771.43 | 885.49 | 733.19 | 885.92 |
| 788.95 | 999.32 | 757.77 | 998.37 |
| 829.12 | 1019.14 | 773.94 | 1016.02 |
| 873.03 | 1028.13 | 875.89 | 1022.83 |
| 880.41 | 1035.85 | 877.21 | 1029.60 |
| 1027.32 | 1106.43 | 1013.70 | 1101.79 |
| 1052.76 | 1177.00 | 1043.50 | 1176.27 |
| 1133.49 | 1216.41 | 1129.12 | 1190.05 |
| 1439.70 | 1220.46 | 1433.77 | 1223.74 |
| 1455.05 | 1267.68 | 1451.34 | 1248.19 |
| 1477.76 | 1276.40 | 1467.35 | 1274.52 |
| 3133.54 | 1340.31 | 3120.46 | 1297.74 |
| 3137.06 | 1364.38 | 3129.47 | 1336.38 |
| 3173.74 | 1378.51 | 3171.21 | 1364.61 |
| | 1389.01 | | 1379.03 |
| | 1397.45 | | 1391.31 |
| | 1403.27 | | 1393.56 |
| | 1422.12 | | 1404.36 |
| | 1436.34 | | 1411.85 |
| | 1451.12 | | 1421.91 |
| | 1463.99 | | 1439.38 |
| | 1481.84 | | 1453.24 |
| | 1489.16 | | 1468.35 |
| | 1521.62 | | 1486.17 |
| | 1547.72 | | 1502.78 |
| | 1597.24 | | 1530.67 |
| | 1630.79 | | 1563.33 |
| | 1670.05 | | 1602.30 |
| | 1710.43 | | 1667.46 |
| | 1779.38 | | 1729.31 |
| | 1866.28 | | 1771.41 |
| | 3061.52 | | 3052.51 |
| | 3062.68 | | 3058.09 |
| | 3079.98 | | 3079.95 |
| | 3170.67 | | 3173.37 |
| | 3179.69 | | 3176.37 |
| | 3197.99 | | 3206.71 |
| | 3221.70 | | 3232.83 |
| | 3251.67 | | 3246.74 |
| | 3591.73 | | 3619.24 |

**$K^+LF$**

| $S_0$ | | $S_1$ | |
|---|---|---|---|
| a'' | a' | a'' | a' |
| 33.28 | 71.25 | 35.14 | 86.20 |
| 53.30 | 154.94 | 48.52 | 161.94 |
| 63.03 | 199.72 | 52.51 | 201.59 |
| 101.23 | 289.03 | 94.57 | 287.33 |
| 134.90 | 299.02 | 112.43 | 294.64 |
| 141.10 | 336.12 | 124.24 | 332.25 |
| 160.82 | 357.19 | 157.08 | 359.95 |
| 175.04 | 414.70 | 173.93 | 421.37 |
| 192.66 | 449.56 | 194.07 | 450.45 |
| 209.95 | 503.87 | 216.74 | 495.40 |
| 252.38 | 525.99 | 234.14 | 528.73 |
| 338.54 | 550.79 | 336.64 | 548.86 |
| 380.45 | 608.75 | 346.57 | 613.03 |
| 457.57 | 643.77 | 414.32 | 637.05 |
| 528.38 | 683.14 | 485.85 | 674.90 |
| 638.46 | 761.81 | 620.38 | 746.07 |
| 678.88 | 794.07 | 645.42 | 788.22 |
| 749.01 | 846.78 | 678.68 | 834.97 |
| 772.13 | 884.78 | 732.54 | 884.78 |
| 787.73 | 999.41 | 757.28 | 998.54 |
| 828.84 | 1020.75 | 772.29 | 1016.98 |
| 873.35 | 1028.00 | 874.19 | 1022.83 |
| 880.70 | 1035.53 | 875.49 | 1028.62 |
| 1027.55 | 1106.46 | 1014.07 | 1101.36 |
| 1053.10 | 1175.68 | 1043.35 | 1175.17 |
| 1133.95 | 1214.19 | 1129.22 | 1187.02 |
| 1440.11 | 1221.46 | 1434.04 | 1222.80 |
| 1455.35 | 1267.09 | 1452.28 | 1244.86 |
| 1478.20 | 1275.12 | 1467.47 | 1271.92 |
| 3132.97 | 1338.20 | 3120.05 | 1296.11 |
| 3136.05 | 1363.92 | 3128.28 | 1332.59 |
| 3172.53 | 1378.62 | 3170.76 | 1364.15 |
| | 1389.26 | | 1377.59 |
| | 1397.44 | | 1391.08 |
| | 1402.91 | | 1393.71 |
| | 1421.19 | | 1402.47 |
| | 1436.36 | | 1411.56 |
| | 1450.53 | | 1421.95 |
| | 1464.07 | | 1438.02 |
| | 1476.99 | | 1452.71 |
| | 1487.38 | | 1468.05 |
| | 1522.16 | | 1485.12 |
| | 1547.34 | | 1498.49 |
| | 1598.63 | | 1531.31 |
| | 1629.97 | | 1561.82 |
| | 1669.58 | | 1595.82 |
| | 1710.69 | | 1663.38 |
| | 1774.86 | | 1725.81 |
| | 1864.14 | | 1766.56 |
| | 3061.00 | | 3051.90 |
| | 3061.84 | | 3057.42 |
| | 3079.43 | | 3080.29 |
| | 3168.33 | | 3172.57 |
| | 3178.54 | | 3173.89 |
| | 3200.43 | | 3208.25 |
| | 3221.63 | | 3234.10 |
| | 3250.50 | | 3247.29 |
| | 3594.23 | | 3620.17 |

## $Rb^+LF$

| $S_0$ | | $S_1$ | |
|---|---|---|---|
| a'' | a' | a'' | a' |
| 27.69 | 48.35 | 29.52 | 59.59 |
| 49.43 | 124.38 | 45.31 | 129.78 |
| 62.77 | 183.28 | 51.22 | 184.94 |
| 101.25 | 286.87 | 93.20 | 285.01 |
| 134.94 | 298.76 | 111.07 | 296.24 |
| 139.16 | 333.44 | 122.99 | 329.65 |
| 159.40 | 357.14 | 155.39 | 360.12 |
| 175.00 | 412.17 | 171.14 | 418.75 |
| 192.60 | 448.92 | 190.75 | 449.73 |
| 209.84 | 503.67 | 216.80 | 494.86 |
| 252.42 | 525.34 | 233.67 | 527.77 |
| 338.41 | 550.12 | 335.37 | 548.31 |
| 380.40 | 608.52 | 346.61 | 612.58 |
| 457.50 | 643.68 | 414.62 | 637.23 |
| 527.81 | 682.45 | 485.87 | 673.84 |
| 638.67 | 761.98 | 621.10 | 746.11 |
| 678.83 | 793.89 | 645.64 | 787.77 |
| 748.37 | 846.25 | 678.70 | 834.19 |
| 772.79 | 884.64 | 733.12 | 884.60 |
| 787.14 | 999.56 | 757.15 | 998.54 |
| 828.79 | 1021.35 | 771.33 | 1017.26 |
| 873.52 | 1028.36 | 873.27 | 1022.88 |
| 882.00 | 1035.55 | 874.37 | 1028.21 |
| 1027.69 | 1106.49 | 1014.62 | 1101.72 |
| 1053.22 | 1175.28 | 1043.54 | 1175.22 |
| 1134.15 | 1213.54 | 1129.31 | 1186.87 |
| 1440.29 | 1222.23 | 1434.71 | 1222.31 |
| 1455.50 | 1267.16 | 1451.73 | 1244.15 |
| 1478.39 | 1274.83 | 1467.33 | 1272.74 |
| 3132.74 | 1337.87 | 3121.10 | 1296.12 |
| 3135.65 | 1363.97 | 3127.38 | 1332.46 |
| 3172.10 | 1378.88 | 3169.31 | 1364.23 |
| | 1389.39 | | 1379.75 |
| | 1397.56 | | 1391.41 |
| | 1403.20 | | 1393.56 |
| | 1420.92 | | 1402.39 |
| | 1436.53 | | 1411.78 |
| | 1450.50 | | 1422.38 |
| | 1464.22 | | 1438.16 |
| | 1474.86 | | 1451.84 |
| | 1487.04 | | 1468.18 |
| | 1522.68 | | 1484.59 |
| | 1547.48 | | 1496.58 |
| | 1599.66 | | 1531.78 |
| | 1630.20 | | 1562.26 |
| | 1670.35 | | 1594.69 |
| | 1711.23 | | 1662.68 |
| | 1778.38 | | 1730.02 |
| | 1863.30 | | 1764.05 |
| | 3060.77 | | 3052.84 |
| | 3061.60 | | 3056.68 |
| | 3079.21 | | 3079.09 |
| | 3167.70 | | 3171.84 |
| | 3178.20 | | 3173.81 |
| | 3203.00 | | 3208.67 |
| | 3221.48 | | 3233.74 |
| | 3250.16 | | 3245.56 |
| | 3596.31 | | 3622.73 |

## $Cs^+LF$

| $S_0$ a'' | $S_0$ a' | $S_1$ a'' | $S_1$ a' |
|---|---|---|---|
| 24.53 | 36.18 | 26.45 | 45.23 |
| 47.98 | 106.71 | 44.41 | 111.28 |
| 63.24 | 177.42 | 51.55 | 178.82 |
| 100.53 | 285.73 | 92.01 | 283.06 |
| 135.61 | 296.81 | 110.42 | 294.32 |
| 138.26 | 331.32 | 124.88 | 327.50 |
| 159.04 | 357.34 | 155.59 | 359.86 |
| 175.36 | 409.88 | 172.01 | 415.68 |
| 194.52 | 448.72 | 193.16 | 449.16 |
| 210.78 | 503.77 | 216.64 | 494.24 |
| 251.98 | 525.09 | 234.41 | 527.09 |
| 338.65 | 549.17 | 335.11 | 547.99 |
| 379.68 | 608.29 | 346.09 | 611.82 |
| 457.37 | 643.61 | 414.29 | 637.22 |
| 526.89 | 681.66 | 485.06 | 673.13 |
| 638.44 | 761.90 | 620.19 | 745.89 |
| 678.84 | 793.90 | 644.64 | 787.38 |
| 748.08 | 845.29 | 678.14 | 833.49 |
| 773.30 | 884.19 | 733.01 | 884.13 |
| 787.03 | 999.95 | 757.30 | 998.65 |
| 829.63 | 1021.47 | 771.70 | 1017.51 |
| 874.58 | 1028.02 | 873.79 | 1022.56 |
| 884.48 | 1035.97 | 874.56 | 1028.16 |
| 1027.67 | 1106.28 | 1014.38 | 1101.42 |
| 1052.86 | 1174.85 | 1043.30 | 1174.59 |
| 1134.63 | 1212.36 | 1129.38 | 1185.38 |
| 1440.37 | 1221.89 | 1434.45 | 1222.12 |
| 1456.16 | 1265.86 | 1452.85 | 1243.50 |
| 1478.52 | 1273.66 | 1467.51 | 1271.27 |
| 3132.24 | 1338.00 | 3120.01 | 1295.11 |
| 3134.66 | 1363.34 | 3127.08 | 1331.85 |
| 3172.58 | 1379.19 | 3169.73 | 1364.31 |
| | 1389.12 | | 1377.80 |
| | 1396.30 | | 1390.94 |
| | 1402.75 | | 1393.79 |
| | 1420.67 | | 1402.13 |
| | 1436.69 | | 1411.96 |
| | 1450.29 | | 1421.98 |
| | 1464.76 | | 1437.64 |
| | 1474.40 | | 1452.03 |
| | 1486.57 | | 1468.08 |
| | 1523.24 | | 1484.62 |
| | 1547.35 | | 1496.70 |
| | 1600.76 | | 1532.39 |
| | 1629.71 | | 1561.31 |
| | 1669.89 | | 1592.47 |
| | 1711.68 | | 1661.65 |
| | 1775.12 | | 1725.79 |
| | 1863.00 | | 1763.29 |
| | 3059.90 | | 3051.90 |
| | 3061.46 | | 3056.62 |
| | 3079.78 | | 3079.83 |
| | 3166.70 | | 3171.88 |
| | 3178.14 | | 3173.18 |
| | 3207.69 | | 3211.63 |
| | 3221.55 | | 3234.35 |
| | 3250.23 | | 3246.61 |
| | 3596.70 | | 3623.06 |

**LF**

| $S_0$ | | $S_1$ | |
|---|---|---|---|
| a'' | a' | a'' | a' |
| 44.12 | 164.63 | -36.80 | 164.70 |
| 63.49 | 278.64 | 47.65 | 276.27 |
| 101.17 | 295.23 | 62.18 | 293.63 |
| 124.45 | 325.76 | 99.41 | 321.95 |
| 136.53 | 354.64 | 125.23 | 357.65 |
| 152.60 | 405.04 | 145.50 | 408.51 |
| 173.49 | 444.67 | 157.24 | 444.31 |
| 192.34 | 502.42 | 186.72 | 489.35 |
| 208.16 | 517.89 | 211.58 | 520.79 |
| 249.83 | 545.57 | 240.34 | 544.73 |
| 334.97 | 606.65 | 321.66 | 602.81 |
| 379.05 | 642.39 | 336.71 | 635.25 |
| 456.38 | 679.87 | 415.38 | 668.92 |
| 519.95 | 763.83 | 477.25 | 742.81 |
| 638.38 | 794.02 | 615.94 | 783.00 |
| 674.99 | 842.21 | 652.15 | 830.00 |
| 731.99 | 883.28 | 674.17 | 878.13 |
| 780.20 | 1000.62 | 738.58 | 999.58 |
| 788.18 | 1020.38 | 761.60 | 1014.18 |
| 836.46 | 1036.16 | 773.10 | 1018.56 |
| 866.02 | 1040.18 | 858.96 | 1026.85 |
| 925.25 | 1108.42 | 899.87 | 1096.28 |
| 1030.99 | 1176.49 | 1019.18 | 1174.61 |
| 1056.48 | 1204.99 | 1043.60 | 1189.12 |
| 1137.55 | 1235.73 | 1130.81 | 1202.07 |
| 1443.48 | 1267.87 | 1438.58 | 1243.78 |
| 1458.75 | 1273.70 | 1453.48 | 1265.39 |
| 1480.40 | 1337.58 | 1467.07 | 1289.83 |
| 3121.66 | 1363.66 | 3109.02 | 1337.17 |
| 3126.09 | 1383.05 | 3115.47 | 1360.96 |
| 3156.35 | 1390.32 | 3149.30 | 1381.40 |
| | 1397.39 | | 1390.85 |
| | 1408.38 | | 1394.29 |
| | 1414.97 | | 1397.55 |
| | 1429.25 | | 1416.21 |
| | 1439.09 | | 1422.54 |
| | 1451.97 | | 1428.25 |
| | 1466.90 | | 1452.73 |
| | 1479.05 | | 1464.10 |
| | 1527.08 | | 1478.06 |
| | 1551.50 | | 1486.67 |
| | 1617.39 | | 1540.63 |
| | 1632.00 | | 1554.83 |
| | 1678.15 | | 1575.29 |
| | 1713.97 | | 1651.06 |
| | 1836.54 | | 1737.38 |
| | 1848.67 | | 1809.22 |
| | 3052.84 | | 3044.10 |
| | 3055.10 | | 3048.55 |
| | 3069.11 | | 3066.56 |
| | 3165.21 | | 3157.68 |
| | 3166.04 | | 3171.41 |
| | 3210.65 | | 3223.92 |
| | 3224.44 | | 3226.81 |
| | 3238.45 | | 3233.27 |
| | 3619.17 | | 3632.26 |

**Table S4.** Selected atomic charges (in e) of $M^+LF(O4+)$ and LF in the $S_0$ and $S_1$ states using natural bond orbital analysis (PBE0/cc-pVDZ).

| | $q_M$ | | $q_{N5}$ | | $q_{O4}$ | | $q_{O2}$ | | $q_{N1}$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_0$ | $S_1$ | $S_0$ | $S_1$ | $S_0$ | $S_1$ | $S_0$ | $S_1$ |
| Li | 0.881 | 0.860 | -0.519 | -0.619 | -0.738 | -0.744 | -0.536 | -0.497 | -0.632 | -0.482 |
| Na | 0.922 | 0.908 | -0.494 | -0.595 | -0.723 | -0.733 | -0.545 | -0.505 | -0.636 | -0.481 |
| K | 0.922 | 0.909 | -0.467 | -0.569 | -0.725 | -0.736 | -0.550 | -0.509 | -0.639 | -0.481 |
| Rb | 0.928 | 0.915 | -0.459 | -0.561 | -0.721 | -0.732 | -0.553 | -0.511 | -0.640 | -0.482 |
| Cs | 0.917 | 0.906 | -0.446 | -0.550 | -0.724 | -0.736 | -0.555 | -0.513 | -0.641 | -0.483 |
| LF | | | -0.376 | -0.454 | -0.577 | -0.592 | -0.598 | -0.570 | -0.660 | -0.508 |

**Table S5.** Vertical transition energies ($\nu$ in $cm^{-1}$, $\lambda$ in nm) and oscillator strength (f) for the first four excited singlet states of $M^+LF(O2)$ with M=Li-Cs and $M^+LF(O2+)$ with M=Li-K calculated at the PBE0/cc-pVDZ level.[a]

| O2 | $S_1$ ($\pi\pi^*$) | | | $S_2$ ($n\pi^*$) | | | $S_3$ ($n\pi^*/\pi\pi^*$) | | | $S_4$ ($n\pi^*/\pi\pi^*$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu$ | $\lambda$ | F | $\nu$ | $\lambda$ | f | $\nu$ | $\lambda$ | f | $\nu$ | $\lambda$ | f |
| Li | 25735 | 388.57 | 0.174 | 27090 | 369.14 | 0.001 | 29171 | 342.81 | 0.263 | 29344 | 340.79 | 0.000 |
| Na | 25746 | 388.41 | 0.193 | 27077 | 369.32 | 0.001 | 29267 | 341.68 | 0.000 | 29581 | 338.06 | 0.240 |
| K | 25698 | 389.14 | 0.204 | 27066 | 369.47 | 0.001 | 29202 | 342.44 | 0.000 | 29722 | 336.45 | 0.234 |
| Rb | 25674 | 389.50 | 0.210 | 27055 | 369.62 | 0.001 | 29162 | 342.91 | 0.000 | 29802 | 335.55 | 0.234 |
| Cs | 25650 | 389.87 | 0.216 | 27039 | 369.83 | 0.001 | 29129 | 343.30 | 0.000 | 29839 | 335.13 | 0.234 |

| O2+ | $S_1$ ($\pi\pi^*$) | | | $S_2$ ($n\pi^*$) | | | $S_3$ ($n\pi^*/\pi\pi^*$) | | | $S_4$ ($n\pi^*/\pi\pi^*$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu$ | $\lambda$ | F | $\nu$ | $\lambda$ | f | $\nu$ | $\lambda$ | f | $\nu$ | $\lambda$ | f |
| Li | 26159 | 382.28 | 0.138 | 27728 | 360.64 | 0.001 | 29175 | 342.76 | 0.303 | 29916 | 334.27 | 0.000 |
| Na | 26191 | 381.81 | 0.165 | 27332 | 365.87 | 0.005 | 29443 | 339.64 | 0.235 | 29762 | 336.00 | 0.040 |
| K | 26063 | 383.69 | 0.191 | 27161 | 368.18 | 0.001 | 29413 | 339.99 | 0.000 | 29697 | 336.73 | 0.250 |

[a] The character of the $S_3$/$S_4$ states depend on the metal. The optically bright $\pi\pi^*$ states have large f values, while the optically dark $n\pi^*$ states have f values close to 0.