

ASSOCIATED CONTENT

Supporting Information.

Table S1. Full list of rotational transitions observed (in MHz) for the parent species of fluoroxene.

| J' | K'_{-1} | K'_{+1} | J'' | K''_{-1} | K''_{+1} | obs. ^a | o.-c. ^b |
|----|---------|---------|-----|----------|----------|-------------------|--------------------|
| 8 | 1 | 8 | 7 | 2 | 5 | 6407.5623 | -0.0070 |
| 3 | 1 | 3 | 2 | 1 | 2 | 6467.4818 | -0.0025 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6542.9786 | -0.0038 |
| 3 | 2 | 2 | 2 | 2 | 1 | 6545.3498 | -0.0039 |
| 3 | 2 | 1 | 2 | 2 | 0 | 6547.7485 | -0.0032 |
| 3 | 1 | 2 | 2 | 1 | 1 | 6622.5104 | -0.0026 |
| 14 | 1 | 13 | 14 | 0 | 14 | 6783.5889 | -0.0027 |
| 11 | 2 | 10 | 10 | 3 | 7 | 7185.9314 | -0.0143 |
| 14 | 3 | 11 | 13 | 4 | 10 | 7271.0895 | -0.0018 |
| 15 | 1 | 14 | 15 | 0 | 15 | 7365.9054 | -0.0104 |
| 11 | 2 | 9 | 10 | 3 | 8 | 7610.3994 | -0.0092 |
| 2 | 1 | 2 | 1 | 0 | 1 | 7626.9890 | -0.0017 |
| 5 | 0 | 5 | 4 | 1 | 4 | 7807.0289 | -0.0071 |
| 3 | 3 | 1 | 4 | 2 | 2 | 7969.2800 | -0.0071 |
| 3 | 3 | 0 | 4 | 2 | 3 | 7978.2675 | -0.0131 |
| 16 | 1 | 15 | 16 | 0 | 16 | 8001.3530 | -0.0061 |
| 6 | 4 | 3 | 7 | 3 | 4 | 8105.2969 | -0.0024 |
| 6 | 4 | 2 | 7 | 3 | 5 | 8106.2079 | -0.0055 |
| 9 | 1 | 9 | 8 | 2 | 6 | 8298.1170 | -0.0081 |
| 8 | 1 | 7 | 7 | 2 | 6 | 8341.0917 | -0.0081 |
| 16 | 2 | 14 | 16 | 1 | 15 | 8382.1935 | 0.0077 |
| 14 | 2 | 12 | 14 | 1 | 13 | 8455.1633 | -0.0004 |
| 19 | 2 | 17 | 19 | 1 | 18 | 8582.2291 | 0.0106 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8622.6110 | -0.0049 |
| 12 | 2 | 10 | 12 | 1 | 11 | 8650.1564 | -0.0156 |
| 17 | 1 | 16 | 17 | 0 | 17 | 8688.5664 | -0.0028 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8721.1732 | -0.0023 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8726.6590 | -0.0050 |
| 4 | 3 | 1 | 3 | 3 | 0 | 8728.2853 | -0.0018 |
| 4 | 3 | 2 | 3 | 3 | 1 | 8728.2853 | -0.0018 |
| 4 | 2 | 2 | 3 | 2 | 1 | 8732.6499 | -0.0056 |
| 11 | 2 | 9 | 11 | 1 | 10 | 8780.0529 | 0.0008 |
| 4 | 1 | 3 | 3 | 1 | 2 | 8829.2950 | -0.0048 |
| 10 | 2 | 8 | 10 | 1 | 9 | 8923.9138 | 0.0083 |
| 9 | 2 | 7 | 9 | 1 | 8 | 9075.9590 | -0.0045 |
| 8 | 2 | 6 | 8 | 1 | 7 | 9230.5879 | -0.0040 |
| 18 | 4 | 15 | 17 | 5 | 12 | 9300.8667 | -0.0093 |
| 7 | 2 | 5 | 7 | 1 | 6 | 9382.4335 | -0.0049 |
| 18 | 1 | 17 | 18 | 0 | 18 | 9425.1993 | -0.0086 |
| 15 | 3 | 12 | 14 | 4 | 11 | 9490.7339 | -0.0158 |
| 6 | 2 | 4 | 6 | 1 | 5 | 9526.5523 | -0.0059 |
| 5 | 2 | 3 | 5 | 1 | 4 | 9658.5119 | 0.0003 |

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|----|---|----|----|---|----|------------|---------|
| 3 | 1 | 3 | 2 | 0 | 2 | 9731.4828 | -0.0025 |
| 4 | 2 | 2 | 4 | 1 | 3 | 9774.4321 | -0.0017 |
| 3 | 2 | 1 | 3 | 1 | 2 | 9871.0754 | -0.0026 |
| 12 | 2 | 10 | 11 | 3 | 9 | 9911.0441 | 0.0038 |
| 2 | 2 | 0 | 2 | 1 | 1 | 9945.8363 | -0.0031 |
| 6 | 0 | 6 | 5 | 1 | 5 | 10099.6868 | -0.0083 |
| 2 | 2 | 1 | 2 | 1 | 2 | 10100.2718 | -0.0015 |
| 3 | 2 | 2 | 3 | 1 | 3 | 10178.1388 | -0.0039 |
| 4 | 2 | 3 | 4 | 1 | 4 | 10282.1868 | -0.0041 |
| 5 | 4 | 2 | 6 | 3 | 3 | 10290.3383 | -0.0152 |
| 5 | 4 | 1 | 6 | 3 | 4 | 10290.7027 | -0.0164 |
| 5 | 2 | 4 | 5 | 1 | 5 | 10412.5935 | -0.0019 |
| 11 | 6 | 5 | 12 | 5 | 8 | 10553.3479 | 0.0022 |
| 11 | 6 | 6 | 12 | 5 | 7 | 10553.3479 | 0.0050 |
| 6 | 2 | 5 | 6 | 1 | 6 | 10569.5582 | -0.0045 |
| 14 | 7 | 7 | 15 | 6 | 10 | 10683.7291 | -0.0070 |
| 14 | 7 | 8 | 15 | 6 | 9 | 10683.7291 | -0.0070 |
| 9 | 1 | 8 | 8 | 2 | 7 | 10744.4276 | 0.0001 |
| 9 | 1 | 8 | 8 | 2 | 7 | 10744.4276 | 0.0001 |
| 7 | 2 | 6 | 7 | 1 | 7 | 10753.3299 | 0.0127 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10777.1580 | -0.0054 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10896.9776 | -0.0016 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10907.5616 | -0.0063 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10919.5277 | -0.0083 |
| 8 | 2 | 7 | 8 | 1 | 8 | 10964.0827 | -0.0073 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11035.4497 | -0.0085 |
| 9 | 2 | 8 | 9 | 1 | 9 | 11202.1070 | 0.0009 |
| 13 | 2 | 12 | 12 | 3 | 9 | 11440.2867 | -0.0016 |
| 10 | 2 | 9 | 10 | 1 | 10 | 11467.5739 | 0.0047 |
| 11 | 2 | 10 | 11 | 1 | 11 | 11760.6520 | 0.0042 |
| 4 | 1 | 4 | 3 | 0 | 3 | 11811.1152 | -0.0035 |
| 11 | 1 | 11 | 10 | 2 | 8 | 11927.0634 | 0.0050 |
| 12 | 2 | 11 | 12 | 1 | 12 | 12081.4649 | 0.0044 |
| 13 | 2 | 11 | 12 | 3 | 10 | 12239.8142 | 0.0049 |
| 13 | 2 | 12 | 13 | 1 | 13 | 12430.0655 | 0.0049 |
| 7 | 5 | 2 | 8 | 4 | 5 | 12607.0387 | 0.0043 |
| 7 | 5 | 3 | 8 | 4 | 4 | 12607.0387 | 0.0043 |
| 10 | 6 | 4 | 11 | 5 | 7 | 12738.7377 | 0.0019 |
| 14 | 2 | 13 | 14 | 1 | 14 | 12806.4230 | 0.0001 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12930.9926 | -0.0042 |
| 6 | 0 | 6 | 5 | 0 | 5 | 13069.8116 | -0.0108 |
| 6 | 5 | 1 | 5 | 5 | 0 | 13091.8962 | 0.0048 |
| 6 | 5 | 2 | 5 | 5 | 1 | 13091.8962 | 0.0048 |
| 6 | 4 | 2 | 5 | 4 | 1 | 13092.5520 | 0.0046 |
| 6 | 4 | 3 | 5 | 4 | 2 | 13092.5520 | 0.0046 |
| 6 | 3 | 4 | 5 | 3 | 3 | 13093.7807 | 0.0048 |

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|----|---|----|----|---|----|------------|---------|
| 6 | 3 | 3 | 5 | 3 | 2 | 13094.0229 | 0.0035 |
| 6 | 2 | 4 | 5 | 2 | 3 | 13108.8583 | -0.0031 |
| 10 | 1 | 9 | 9 | 2 | 8 | 13169.6460 | 0.0029 |
| 15 | 2 | 14 | 15 | 1 | 15 | 13210.4370 | 0.0056 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13240.8119 | -0.0029 |
| 3 | 2 | 2 | 3 | 0 | 3 | 13366.6374 | -0.0083 |
| 4 | 2 | 3 | 4 | 0 | 4 | 13372.1359 | 0.0016 |
| 5 | 2 | 4 | 5 | 0 | 5 | 13382.7022 | -0.0207 |
| 6 | 2 | 5 | 6 | 0 | 6 | 13400.8556 | -0.0088 |
| 8 | 2 | 7 | 8 | 0 | 8 | 13471.7434 | 0.0030 |
| 9 | 2 | 8 | 9 | 0 | 9 | 13531.3167 | 0.0094 |
| 14 | 2 | 13 | 13 | 3 | 10 | 13543.2659 | 0.0003 |
| 16 | 2 | 15 | 16 | 1 | 16 | 13641.8674 | -0.0010 |
| 12 | 1 | 12 | 11 | 2 | 9 | 13655.5661 | 0.0005 |
| 17 | 3 | 15 | 16 | 4 | 12 | 13795.2119 | 0.0038 |
| 5 | 1 | 5 | 4 | 0 | 4 | 13867.1136 | 0.0069 |
| 17 | 3 | 14 | 16 | 4 | 13 | 13962.4294 | 0.0043 |
| 17 | 2 | 16 | 17 | 1 | 17 | 14100.4103 | 0.0029 |
| 2 | 2 | 1 | 1 | 1 | 0 | 14360.5015 | -0.0011 |
| 2 | 2 | 0 | 1 | 1 | 1 | 14412.7792 | -0.0009 |
| 18 | 2 | 17 | 18 | 1 | 18 | 14585.6108 | 0.0044 |
| 14 | 2 | 12 | 13 | 3 | 11 | 14599.2154 | -0.0006 |
| 8 | 0 | 8 | 7 | 1 | 7 | 14728.4164 | 0.0114 |
| 6 | 5 | 1 | 7 | 4 | 4 | 14790.9718 | 0.0033 |
| 6 | 5 | 2 | 7 | 4 | 3 | 14790.9718 | 0.0033 |
| 19 | 3 | 16 | 19 | 2 | 17 | 14909.8798 | -0.0101 |
| 9 | 6 | 3 | 10 | 5 | 6 | 14923.4116 | -0.0001 |
| 12 | 7 | 5 | 13 | 6 | 8 | 15054.9970 | 0.0014 |
| 12 | 7 | 6 | 13 | 6 | 7 | 15054.9970 | 0.0014 |
| 7 | 1 | 7 | 6 | 1 | 6 | 15083.9999 | 0.0032 |
| 19 | 2 | 18 | 19 | 1 | 19 | 15096.9094 | 0.0032 |
| 18 | 3 | 15 | 18 | 2 | 16 | 15170.2551 | -0.0016 |
| 7 | 0 | 7 | 6 | 0 | 6 | 15239.1699 | 0.0019 |
| 7 | 2 | 6 | 6 | 2 | 5 | 15267.7549 | 0.0039 |
| 7 | 6 | 1 | 6 | 6 | 0 | 15273.6125 | -0.0001 |
| 7 | 5 | 2 | 6 | 5 | 1 | 15274.2290 | 0.0015 |
| 7 | 5 | 3 | 6 | 5 | 2 | 15274.2290 | 0.0015 |
| 7 | 4 | 3 | 6 | 4 | 2 | 15275.2237 | 0.0036 |
| 7 | 4 | 4 | 6 | 4 | 3 | 15275.2237 | 0.0036 |
| 7 | 3 | 5 | 6 | 3 | 4 | 15277.0580 | 0.0045 |
| 7 | 3 | 4 | 6 | 3 | 3 | 15277.6064 | 0.0053 |
| 7 | 2 | 5 | 6 | 2 | 4 | 15301.0673 | 0.0022 |
| 13 | 1 | 13 | 12 | 2 | 10 | 15320.2480 | 0.0029 |
| 17 | 3 | 14 | 17 | 2 | 15 | 15415.3392 | -0.0007 |
| 7 | 1 | 6 | 6 | 1 | 5 | 15445.1918 | 0.0070 |
| 11 | 1 | 10 | 10 | 2 | 9 | 15615.7749 | 0.0018 |

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| 20 | 2 | 19 | 20 | 1 | 20 | 15633.6343 | 0.0034 |
| 16 | 3 | 13 | 16 | 2 | 14 | 15641.2234 | 0.0018 |
| 15 | 3 | 12 | 15 | 2 | 13 | 15844.9765 | -0.0020 |
| 6 | 1 | 6 | 5 | 0 | 5 | 15901.1280 | 0.0037 |
| 14 | 3 | 11 | 14 | 2 | 12 | 16024.7405 | -0.0004 |
| 13 | 3 | 10 | 13 | 2 | 11 | 16179.6936 | 0.0002 |
| 18 | 3 | 15 | 17 | 4 | 14 | 16218.8242 | 0.0115 |
| 12 | 3 | 9 | 12 | 2 | 10 | 16310.0175 | 0.0001 |
| 11 | 3 | 8 | 11 | 2 | 9 | 16416.7789 | 0.0014 |
| 3 | 2 | 2 | 2 | 1 | 1 | 16490.5909 | -0.0025 |
| 10 | 3 | 7 | 10 | 2 | 8 | 16501.7619 | 0.0014 |
| 9 | 3 | 6 | 9 | 2 | 7 | 16567.2875 | 0.0031 |
| 8 | 3 | 5 | 8 | 2 | 6 | 16616.0035 | 0.0029 |
| 3 | 2 | 1 | 2 | 1 | 2 | 16648.6296 | 0.0048 |
| 7 | 3 | 4 | 7 | 2 | 5 | 16650.7115 | 0.0075 |
| 6 | 3 | 3 | 6 | 2 | 4 | 16674.1728 | 0.0048 |
| 5 | 3 | 2 | 5 | 2 | 3 | 16689.0182 | 0.0081 |
| 4 | 3 | 1 | 4 | 2 | 2 | 16697.6027 | 0.0110 |
| 3 | 3 | 0 | 3 | 2 | 1 | 16701.9529 | 0.0057 |
| 4 | 3 | 2 | 4 | 2 | 3 | 16706.5450 | -0.0053 |
| 5 | 3 | 3 | 5 | 2 | 4 | 16709.8531 | 0.0075 |
| 6 | 3 | 4 | 6 | 2 | 5 | 16715.6628 | 0.0055 |
| 7 | 3 | 5 | 7 | 2 | 6 | 16724.9637 | 0.0040 |
| 8 | 3 | 6 | 8 | 2 | 7 | 16738.8614 | 0.0043 |
| 9 | 3 | 7 | 9 | 2 | 8 | 16758.5730 | 0.0036 |
| 10 | 3 | 8 | 10 | 2 | 9 | 16785.4168 | 0.0004 |
| 11 | 3 | 9 | 11 | 2 | 10 | 16820.8013 | 0.0009 |
| 12 | 3 | 10 | 12 | 2 | 11 | 16866.1908 | 0.0035 |
| 14 | 1 | 14 | 13 | 2 | 11 | 16916.5343 | -0.0016 |
| 13 | 3 | 11 | 13 | 2 | 12 | 16923.0896 | 0.0015 |
| 5 | 5 | 0 | 6 | 4 | 3 | 16974.2961 | -0.0011 |
| 5 | 5 | 1 | 6 | 4 | 2 | 16974.2961 | -0.0011 |
| 15 | 2 | 13 | 14 | 3 | 12 | 16991.2010 | -0.0009 |
| 14 | 3 | 12 | 14 | 2 | 13 | 16993.0360 | -0.0024 |
| 9 | 0 | 9 | 8 | 1 | 8 | 17057.8817 | 0.0040 |
| 15 | 3 | 13 | 15 | 2 | 14 | 17077.5760 | -0.0035 |
| 8 | 6 | 2 | 9 | 5 | 5 | 17107.4741 | -0.0014 |
| 8 | 6 | 3 | 9 | 5 | 4 | 17107.4741 | -0.0014 |
| 16 | 3 | 14 | 16 | 2 | 15 | 17178.2326 | -0.0054 |
| 8 | 1 | 8 | 7 | 1 | 7 | 17236.0595 | 0.0043 |
| 17 | 3 | 15 | 17 | 2 | 16 | 17296.5017 | -0.0052 |
| 8 | 0 | 8 | 7 | 0 | 7 | 17404.5415 | 0.0062 |
| 8 | 2 | 7 | 7 | 2 | 6 | 17446.8302 | 0.0021 |
| 8 | 7 | 1 | 7 | 7 | 0 | 17455.2440 | -0.0034 |
| 8 | 7 | 2 | 7 | 7 | 1 | 17455.2440 | -0.0034 |
| 8 | 6 | 2 | 7 | 6 | 1 | 17455.8609 | -0.0065 |

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|----|---|----|----|---|----|------------|---------|
| 8 | 5 | 3 | 7 | 5 | 2 | 17456.7268 | -0.0001 |
| 8 | 4 | 4 | 7 | 4 | 3 | 17458.1619 | -0.0039 |
| 8 | 3 | 6 | 7 | 3 | 5 | 17460.7267 | 0.0012 |
| 8 | 3 | 5 | 7 | 3 | 4 | 17461.8209 | 0.0011 |
| 8 | 2 | 6 | 7 | 2 | 5 | 17496.5269 | 0.0037 |
| 19 | 3 | 17 | 19 | 2 | 18 | 17591.5712 | -0.0046 |
| 8 | 1 | 7 | 7 | 1 | 6 | 17648.3724 | 0.0026 |
| 16 | 2 | 15 | 15 | 3 | 12 | 17685.1910 | -0.0023 |
| 7 | 1 | 7 | 6 | 0 | 6 | 17915.3044 | 0.0060 |
| 12 | 1 | 11 | 11 | 2 | 10 | 18081.6694 | 0.0008 |

^aObserved frequency; ^bObserved-Calculated

Table S2. Full list of rotational transitions observed (in MHz) for the $^{13}\text{C}_1$ monosubstituted species of fluoroxene

| J' | K' ₋₁ | K' ₊₁ | J'' | K'' ₋₁ | K'' ₊₁ | obs. ^a | o.-c. ^b |
|----|------------------|------------------|-----|-------------------|-------------------|-------------------|--------------------|
| 3 | 0 | 3 | 2 | 0 | 2 | 6403.1692 | -0.0017 |
| 3 | 2 | 2 | 2 | 2 | 1 | 6405.4365 | -0.0029 |
| 3 | 1 | 2 | 2 | 1 | 1 | 6480.9811 | -0.0033 |
| 2 | 1 | 2 | 1 | 0 | 1 | 7539.8187 | 0.0001 |
| 5 | 0 | 5 | 4 | 1 | 4 | 7564.7591 | -0.0090 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8438.2871 | -0.0010 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8534.8757 | -0.0041 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8540.1310 | -0.0006 |
| 4 | 3 | 1 | 3 | 3 | 0 | 8541.6851 | 0.0019 |
| 4 | 3 | 2 | 3 | 3 | 1 | 8541.6851 | 0.0019 |
| 4 | 2 | 2 | 3 | 2 | 1 | 8545.8605 | -0.0058 |
| 4 | 1 | 3 | 3 | 1 | 2 | 8640.6223 | -0.0032 |
| 8 | 2 | 6 | 8 | 1 | 7 | 9257.6625 | -0.0076 |
| 6 | 2 | 4 | 6 | 1 | 5 | 9549.4089 | 0.0118 |
| 3 | 1 | 3 | 2 | 0 | 2 | 9599.2919 | -0.0038 |
| 5 | 2 | 3 | 5 | 1 | 4 | 9679.0858 | 0.0057 |
| 4 | 2 | 2 | 4 | 1 | 3 | 9792.8533 | -0.0020 |
| 6 | 0 | 6 | 5 | 1 | 5 | 9808.8561 | 0.0014 |
| 3 | 2 | 1 | 3 | 1 | 2 | 9887.6136 | -0.0010 |
| 2 | 2 | 0 | 2 | 1 | 1 | 9960.8570 | -0.0074 |
| 2 | 2 | 1 | 2 | 1 | 2 | 10112.0598 | -0.0033 |
| 3 | 2 | 2 | 3 | 1 | 3 | 10188.2861 | 0.0000 |
| 4 | 2 | 3 | 4 | 1 | 4 | 10290.1271 | -0.0024 |
| 5 | 2 | 4 | 5 | 1 | 5 | 10417.7661 | 0.0020 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10546.7999 | -0.0001 |
| 6 | 2 | 5 | 6 | 1 | 6 | 10571.3963 | 0.0083 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10664.2937 | -0.0074 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10674.4315 | -0.0030 |
| 5 | 4 | 2 | 4 | 4 | 1 | 10676.8468 | -0.0101 |
| 5 | 4 | 1 | 4 | 4 | 0 | 10676.8468 | -0.0101 |
| 5 | 3 | 2 | 4 | 3 | 1 | 10677.6672 | -0.0053 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10685.8835 | -0.0068 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10799.6696 | 0.0039 |
| 4 | 1 | 4 | 3 | 0 | 3 | 11634.4106 | -0.0023 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12654.6302 | 0.0028 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12790.8716 | -0.0149 |
| 6 | 2 | 5 | 5 | 2 | 4 | 12808.2485 | -0.0026 |
| 6 | 4 | 2 | 5 | 4 | 1 | 12812.6388 | 0.0075 |
| 6 | 4 | 3 | 5 | 4 | 2 | 12812.6388 | 0.0075 |
| 6 | 3 | 4 | 5 | 3 | 3 | 12813.8139 | 0.0005 |
| 6 | 3 | 3 | 5 | 3 | 2 | 12814.0423 | 0.0010 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12828.2693 | 0.0134 |

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| 6 | 1 | 5 | 5 | 1 | 4 | 12957.9404 | 0.0016 |
| 5 | 1 | 5 | 4 | 0 | 4 | 13646.3425 | 0.0093 |
| 2 | 2 | 1 | 1 | 1 | 0 | 14281.1862 | -0.0039 |
| 2 | 2 | 0 | 1 | 1 | 1 | 14332.3524 | -0.0025 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14761.6538 | -0.0008 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14914.1138 | -0.0056 |
| 7 | 2 | 6 | 6 | 2 | 5 | 14941.4838 | -0.0003 |
| 7 | 5 | 3 | 6 | 5 | 2 | 14947.6835 | 0.0141 |
| 7 | 5 | 2 | 6 | 5 | 1 | 14947.6835 | 0.0141 |
| 7 | 4 | 3 | 6 | 4 | 2 | 14948.6332 | 0.0079 |
| 7 | 4 | 4 | 6 | 4 | 3 | 14948.6332 | 0.0079 |
| 7 | 3 | 5 | 6 | 3 | 4 | 14950.3921 | 0.0019 |
| 7 | 3 | 4 | 6 | 3 | 3 | 14950.9040 | 0.0013 |
| 7 | 2 | 5 | 6 | 2 | 4 | 14973.3794 | -0.0008 |
| 7 | 1 | 6 | 6 | 1 | 5 | 15115.2680 | -0.0008 |
| 6 | 1 | 6 | 5 | 0 | 5 | 15636.6565 | -0.0027 |
| 2 | 3 | 9 | 12 | 2 | 10 | 16348.1634 | -0.0006 |
| 3 | 2 | 2 | 2 | 1 | 1 | 16365.7371 | 0.0071 |
| 3 | 2 | 1 | 2 | 1 | 2 | 16520.3769 | 0.0052 |
| 9 | 3 | 6 | 9 | 2 | 7 | 16595.3813 | 0.0080 |
| 9 | 0 | 9 | 8 | 1 | 8 | 16621.1875 | -0.0069 |
| 8 | 3 | 5 | 8 | 2 | 6 | 16642.0887 | 0.0010 |
| 4 | 3 | 1 | 4 | 2 | 2 | 16720.2539 | -0.0017 |
| 4 | 3 | 2 | 4 | 2 | 3 | 16728.8143 | -0.0165 |
| 5 | 3 | 3 | 5 | 2 | 4 | 16731.9779 | -0.0054 |
| 6 | 3 | 4 | 6 | 2 | 5 | 16737.5425 | -0.0031 |
| 7 | 3 | 5 | 7 | 2 | 6 | 16746.4581 | 0.0063 |
| 9 | 3 | 7 | 9 | 2 | 8 | 16778.6511 | 0.0066 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16867.7779 | -0.0004 |
| 8 | 0 | 8 | 7 | 0 | 7 | 17033.5313 | -0.0036 |
| 8 | 2 | 7 | 7 | 2 | 6 | 17074.0384 | 0.0011 |
| 8 | 5 | 3 | 7 | 5 | 2 | 17083.5090 | 0.0127 |
| 8 | 5 | 4 | 7 | 5 | 3 | 17083.5090 | 0.0127 |
| 8 | 4 | 4 | 7 | 4 | 3 | 17084.8797 | 0.0037 |
| 8 | 4 | 5 | 7 | 4 | 4 | 17084.8797 | 0.0037 |
| 8 | 3 | 6 | 7 | 3 | 5 | 17087.3506 | 0.0042 |
| 8 | 3 | 5 | 7 | 3 | 4 | 17088.3735 | 0.0030 |
| 8 | 2 | 6 | 7 | 2 | 5 | 17121.6287 | 0.0001 |
| 8 | 1 | 7 | 7 | 1 | 6 | 17271.4650 | -0.0019 |
| 7 | 1 | 7 | 6 | 0 | 6 | 17607.4246 | -0.0027 |
| 4 | 2 | 3 | 3 | 1 | 2 | 18424.8725 | -0.0046 |

^aObserved frequency; ^bObserved-Calculated

Table S3. Full list of rotational transitions observed (in MHz) for the $^{13}\text{C}_2$ monosubstituted species of fluoroxene

| J' | K'_{-1} | K'_{+1} | J'' | K''_{-1} | K''_{+1} | obs. ^a | o.-c. ^b |
|----|---------|---------|-----|----------|----------|-------------------|--------------------|
| 3 | 1 | 3 | 2 | 1 | 2 | 6380.9687 | 0.0007 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6455.1686 | -0.0008 |
| 3 | 2 | 2 | 2 | 2 | 1 | 6457.4486 | -0.0034 |
| 3 | 2 | 1 | 2 | 2 | 0 | 6459.7430 | -0.0182 |
| 3 | 1 | 2 | 2 | 1 | 1 | 6533.2500 | -0.0036 |
| 2 | 1 | 2 | 1 | 0 | 1 | 7576.5366 | -0.0003 |
| 5 | 0 | 5 | 4 | 1 | 4 | 7649.8983 | -0.0042 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8507.2871 | 0.0010 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8604.1924 | -0.0023 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8609.4768 | -0.0021 |
| 4 | 3 | 1 | 3 | 3 | 0 | 8611.0438 | 0.0035 |
| 4 | 3 | 2 | 3 | 3 | 1 | 8611.0438 | 0.0035 |
| 4 | 2 | 2 | 3 | 2 | 1 | 8615.2399 | -0.0090 |
| 4 | 1 | 3 | 3 | 1 | 2 | 8710.3111 | -0.0026 |
| 9 | 2 | 7 | 9 | 1 | 8 | 9108.9080 | -0.0073 |
| 8 | 2 | 6 | 8 | 1 | 7 | 9262.2718 | -0.0082 |
| 7 | 2 | 5 | 7 | 1 | 6 | 9412.4863 | -0.0016 |
| 3 | 1 | 3 | 2 | 0 | 2 | 9653.0917 | -0.0023 |
| 5 | 2 | 3 | 5 | 1 | 4 | 9684.8310 | 0.0011 |
| 4 | 2 | 2 | 4 | 1 | 3 | 9798.9603 | 0.0017 |
| 3 | 2 | 1 | 3 | 1 | 2 | 9894.0303 | 0.0068 |
| 6 | 0 | 6 | 5 | 1 | 5 | 9911.6466 | -0.0042 |
| 2 | 2 | 0 | 2 | 1 | 1 | 9967.5172 | 0.0013 |
| 2 | 2 | 1 | 2 | 1 | 2 | 10119.2309 | 0.0021 |
| 3 | 2 | 2 | 3 | 1 | 3 | 10195.7120 | -0.0008 |
| 4 | 2 | 3 | 4 | 1 | 4 | 10297.9019 | -0.0038 |
| 5 | 2 | 4 | 5 | 1 | 5 | 10425.9822 | 0.0031 |
| 6 | 2 | 5 | 6 | 1 | 6 | 10580.1357 | 0.0037 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10633.0432 | 0.0020 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10750.9142 | -0.0043 |
| 7 | 2 | 6 | 7 | 1 | 7 | 10760.5719 | -0.0104 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10761.1185 | 0.0041 |
| 5 | 4 | 2 | 4 | 4 | 1 | 10763.5378 | -0.0146 |
| 5 | 4 | 1 | 4 | 4 | 0 | 10763.5378 | -0.0146 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10772.6341 | -0.0063 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10886.7721 | 0.0030 |
| 4 | 1 | 4 | 3 | 0 | 3 | 11705.2100 | -0.0007 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12758.1133 | 0.0058 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12894.7812 | -0.0080 |
| 6 | 2 | 5 | 5 | 2 | 4 | 12912.2561 | -0.0042 |
| 6 | 5 | 1 | 5 | 5 | 0 | 12916.0387 | 0.0062 |
| 6 | 4 | 2 | 5 | 4 | 1 | 12916.6775 | 0.0092 |

| | | | | | | | |
|----|---|----|----|---|----|------------|---------|
| 6 | 4 | 3 | 5 | 4 | 2 | 12916.6775 | 0.0092 |
| 6 | 3 | 4 | 5 | 3 | 3 | 12917.8597 | 0.0027 |
| 6 | 3 | 3 | 5 | 3 | 2 | 12918.0886 | 0.0017 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13062.4598 | 0.0072 |
| 5 | 1 | 5 | 4 | 0 | 4 | 13734.0565 | -0.0005 |
| 2 | 2 | 1 | 1 | 1 | 0 | 14322.6859 | 0.0002 |
| 2 | 2 | 0 | 1 | 1 | 1 | 14374.0262 | -0.0004 |
| 8 | 0 | 8 | 7 | 1 | 7 | 14478.4136 | 0.0058 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14882.3704 | 0.0012 |
| 7 | 0 | 7 | 6 | 0 | 6 | 15035.2868 | -0.0007 |
| 7 | 2 | 6 | 6 | 2 | 5 | 15062.8220 | 0.0025 |
| 7 | 4 | 4 | 6 | 4 | 3 | 15070.0130 | 0.0074 |
| 7 | 4 | 3 | 6 | 4 | 2 | 15070.0130 | 0.0074 |
| 7 | 3 | 5 | 6 | 3 | 4 | 15071.7833 | 0.0033 |
| 7 | 3 | 4 | 6 | 3 | 3 | 15072.3000 | 0.0031 |
| 7 | 2 | 5 | 6 | 2 | 4 | 15094.9102 | 0.0001 |
| 7 | 1 | 6 | 6 | 1 | 5 | 15237.1772 | -0.0099 |
| 6 | 1 | 6 | 5 | 0 | 5 | 15741.2475 | 0.0015 |
| 3 | 2 | 2 | 2 | 1 | 1 | 16424.3917 | 0.0012 |
| 14 | 1 | 14 | 13 | 2 | 11 | 16565.2264 | 0.0004 |
| 3 | 2 | 1 | 2 | 1 | 2 | 16579.5690 | 0.0015 |
| 7 | 3 | 4 | 7 | 2 | 5 | 16686.5397 | -0.0049 |
| 5 | 3 | 2 | 5 | 2 | 3 | 16723.4583 | -0.0002 |
| 4 | 3 | 1 | 4 | 2 | 2 | 16731.7291 | 0.0028 |
| 4 | 3 | 2 | 4 | 2 | 3 | 16740.3442 | -0.0098 |
| 6 | 3 | 4 | 6 | 2 | 5 | 16749.1247 | 0.0020 |
| 8 | 3 | 6 | 8 | 2 | 7 | 16771.4810 | 0.0078 |
| 9 | 0 | 9 | 8 | 1 | 8 | 16777.0605 | -0.0015 |
| 9 | 3 | 7 | 9 | 2 | 8 | 16790.4783 | 0.0075 |
| 8 | 1 | 8 | 7 | 1 | 7 | 17005.7212 | -0.0008 |
| 8 | 0 | 8 | 7 | 0 | 7 | 17171.9448 | -0.0012 |
| 8 | 2 | 7 | 7 | 2 | 6 | 17212.6994 | 0.0050 |
| 8 | 4 | 4 | 7 | 4 | 3 | 17223.6048 | 0.0038 |
| 8 | 4 | 5 | 7 | 4 | 4 | 17223.6048 | 0.0038 |
| 8 | 3 | 6 | 7 | 3 | 5 | 17226.0824 | -0.0020 |
| 8 | 3 | 5 | 7 | 3 | 4 | 17227.1207 | 0.0031 |
| 8 | 2 | 6 | 7 | 2 | 5 | 17260.5719 | -0.0026 |
| 8 | 1 | 7 | 7 | 1 | 6 | 17410.7793 | -0.0031 |
| 7 | 1 | 7 | 6 | 0 | 6 | 17728.8279 | 0.0021 |

^aObserved frequency; ^bObserved-Calculated

Table S4. Full list of rotational transitions observed (in MHz) for the $^{18}\text{O}_3$ monosubstituted species of fluoroxene

| J' | K'_{-1} | K'_{+1} | J'' | K''_{-1} | K''_{+1} | obs. ^a | o.-c. ^b |
|----|---------|---------|-----|----------|----------|-------------------|--------------------|
| 3 | 1 | 3 | 2 | 1 | 2 | 6423.5394 | -0.0020 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6500.8317 | 0.0004 |
| 3 | 2 | 2 | 2 | 2 | 1 | 6503.3425 | 0.0012 |
| 3 | 2 | 1 | 2 | 2 | 0 | 6505.8948 | 0.0168 |
| 3 | 1 | 2 | 2 | 1 | 1 | 6582.3800 | -0.0075 |
| 2 | 1 | 2 | 1 | 0 | 1 | 7571.8102 | -0.0035 |
| 5 | 0 | 5 | 4 | 1 | 4 | 7767.5153 | -0.0023 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8563.9844 | -0.0014 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8664.8108 | -0.0018 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8670.6201 | -0.0003 |
| 4 | 2 | 2 | 3 | 2 | 1 | 8676.9576 | -0.0005 |
| 5 | 2 | 3 | 5 | 1 | 4 | 9574.5493 | 0.0073 |
| 3 | 1 | 3 | 2 | 0 | 2 | 9660.4038 | -0.0045 |
| 4 | 2 | 2 | 4 | 1 | 3 | 9692.8760 | -0.0002 |
| 3 | 2 | 1 | 3 | 1 | 2 | 9791.6662 | -0.0096 |
| 2 | 2 | 0 | 2 | 1 | 1 | 9868.1784 | -0.0072 |
| 2 | 2 | 1 | 2 | 1 | 2 | 10026.4035 | 0.0007 |
| 6 | 0 | 6 | 5 | 1 | 5 | 10048.3016 | 0.0025 |
| 4 | 2 | 3 | 4 | 1 | 4 | 10212.8355 | -0.0015 |
| 5 | 2 | 4 | 5 | 1 | 5 | 10346.4927 | -0.0010 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10703.8095 | -0.0040 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10826.2647 | -0.0032 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10837.4663 | -0.0038 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10850.1235 | -0.0052 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10968.4698 | 0.0067 |
| 4 | 1 | 4 | 3 | 0 | 3 | 11723.5594 | -0.0035 |
| 7 | 0 | 7 | 6 | 1 | 6 | 12344.6289 | -0.0123 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12984.6032 | 0.0083 |
| 6 | 2 | 5 | 5 | 2 | 4 | 13003.7846 | 0.0016 |
| 6 | 4 | 2 | 5 | 4 | 1 | 13008.6485 | 0.0076 |
| 6 | 3 | 3 | 5 | 3 | 2 | 13010.1999 | 0.0034 |
| 6 | 2 | 4 | 5 | 2 | 3 | 13025.8805 | -0.0024 |
| 5 | 1 | 5 | 4 | 0 | 4 | 13762.5728 | 0.0089 |
| 2 | 2 | 0 | 1 | 1 | 1 | 14309.6639 | 0.0006 |
| 8 | 0 | 8 | 7 | 1 | 7 | 14653.2266 | -0.0040 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14981.0825 | -0.0004 |
| 7 | 0 | 7 | 6 | 0 | 6 | 15139.2296 | -0.0001 |
| 7 | 2 | 6 | 6 | 2 | 5 | 15169.4533 | 0.0011 |
| 7 | 3 | 5 | 6 | 3 | 4 | 15179.2942 | 0.0064 |
| 7 | 3 | 4 | 6 | 3 | 3 | 15179.8924 | 0.0066 |
| 7 | 2 | 5 | 6 | 2 | 4 | 15204.6765 | 0.0015 |
| 7 | 1 | 6 | 6 | 1 | 5 | 15351.1283 | -0.0006 |

| | | | | | | | |
|---|---|---|---|---|---|------------|---------|
| 6 | 1 | 6 | 5 | 0 | 5 | 15779.1752 | -0.0082 |
| 3 | 2 | 2 | 2 | 1 | 1 | 16370.9049 | 0.0124 |
| 3 | 2 | 1 | 2 | 1 | 2 | 16532.9146 | -0.0004 |
| 8 | 1 | 8 | 7 | 1 | 7 | 17118.2870 | -0.0001 |
| 8 | 0 | 8 | 7 | 0 | 7 | 17289.6709 | -0.0014 |
| 8 | 2 | 7 | 7 | 2 | 6 | 17334.3699 | -0.0013 |
| 8 | 3 | 6 | 7 | 3 | 5 | 17349.0617 | 0.0028 |
| 8 | 1 | 7 | 7 | 1 | 6 | 17540.6813 | -0.0005 |
| 7 | 1 | 7 | 6 | 0 | 6 | 17775.6639 | -0.0075 |

^aObserved frequency; ^bObserved-Calculated

Table S5. Full list of rotational transitions observed (in MHz) for the $^{13}\text{C}_4$ monosubstituted species of fluoroxene

| J' | K'_{-1} | K'_{+1} | J'' | K''_{-1} | K''_{+1} | obs. ^a | o.-c. ^b |
|------|-----------|-----------|-------|------------|------------|-------------------|--------------------|
| 3 | 1 | 3 | 2 | 1 | 2 | 6463.4831 | -0.0010 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6539.7710 | -0.0008 |
| 3 | 2 | 1 | 2 | 2 | 0 | 6544.6585 | -0.0012 |
| 3 | 1 | 2 | 2 | 1 | 1 | 6620.1878 | -0.0043 |
| 2 | 1 | 2 | 1 | 0 | 1 | 7614.3904 | -0.0016 |
| 5 | 0 | 5 | 4 | 1 | 4 | 7813.7530 | -0.0087 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8617.2646 | -0.0007 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8716.8262 | 0.0005 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8722.4557 | 0.0049 |
| 4 | 3 | 1 | 3 | 3 | 0 | 8724.1119 | -0.0031 |
| 4 | 3 | 2 | 3 | 3 | 1 | 8724.1119 | -0.0031 |
| 4 | 1 | 3 | 3 | 1 | 2 | 8826.1888 | 0.0013 |
| 7 | 2 | 5 | 7 | 1 | 6 | 9347.6773 | -0.0067 |
| 6 | 2 | 4 | 6 | 1 | 5 | 9492.8584 | 0.0021 |
| 5 | 2 | 3 | 5 | 1 | 4 | 9625.9168 | -0.0010 |
| 3 | 1 | 3 | 2 | 0 | 2 | 9717.0002 | -0.0019 |
| 4 | 2 | 2 | 4 | 1 | 3 | 9742.9121 | 0.0016 |
| 3 | 2 | 1 | 3 | 1 | 2 | 9840.5087 | 0.0011 |
| 2 | 2 | 0 | 2 | 1 | 1 | 9916.0386 | -0.0012 |
| 2 | 2 | 1 | 2 | 1 | 2 | 10072.1412 | 0.0027 |
| 6 | 0 | 6 | 5 | 1 | 5 | 10106.3129 | -0.0056 |
| 3 | 2 | 2 | 3 | 1 | 3 | 10150.8565 | -0.0002 |
| 4 | 2 | 3 | 4 | 1 | 4 | 10256.0450 | 0.0029 |
| 5 | 2 | 4 | 5 | 1 | 5 | 10387.8762 | -0.0001 |
| 6 | 2 | 5 | 6 | 1 | 6 | 10546.5699 | -0.0002 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10770.4503 | 0.0017 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10891.4316 | -0.0001 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10902.2895 | 0.0066 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10914.5417 | -0.0046 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11031.5366 | -0.0022 |
| 4 | 1 | 4 | 3 | 0 | 3 | 11794.4966 | 0.0008 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12922.9020 | 0.0011 |
| 6 | 0 | 6 | 5 | 0 | 5 | 13063.0132 | 0.0078 |
| 6 | 2 | 5 | 5 | 2 | 4 | 13081.6029 | 0.0082 |
| 6 | 2 | 4 | 5 | 2 | 3 | 13103.0074 | 0.0009 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13236.0674 | -0.0007 |
| 5 | 1 | 5 | 4 | 0 | 4 | 13848.1271 | 0.0084 |
| 2 | 2 | 1 | 1 | 1 | 0 | 14329.1499 | 0.0026 |
| 2 | 2 | 0 | 1 | 1 | 1 | 14381.9981 | -0.0013 |
| 7 | 1 | 7 | 6 | 1 | 6 | 15074.4994 | -0.0005 |
| 7 | 0 | 7 | 6 | 0 | 6 | 15230.9994 | 0.0012 |
| 7 | 2 | 6 | 6 | 2 | 5 | 15260.2844 | 0.0018 |

| | | | | | | | |
|---|---|---|---|---|---|------------|---------|
| 7 | 3 | 4 | 6 | 3 | 3 | 15270.3817 | -0.0003 |
| 7 | 2 | 5 | 6 | 2 | 4 | 15294.4149 | 0.0016 |
| 7 | 1 | 6 | 6 | 1 | 5 | 15439.5881 | 0.0026 |
| 6 | 1 | 6 | 5 | 0 | 5 | 15879.5878 | 0.0000 |
| 3 | 2 | 2 | 2 | 1 | 1 | 16457.6286 | 0.0007 |
| 8 | 3 | 5 | 8 | 2 | 6 | 16565.5689 | -0.0013 |
| 7 | 3 | 4 | 7 | 2 | 5 | 16601.1083 | 0.0047 |
| 3 | 2 | 1 | 2 | 1 | 2 | 16617.4137 | 0.0010 |
| 6 | 3 | 3 | 6 | 2 | 4 | 16625.1342 | -0.0006 |
| 5 | 3 | 2 | 5 | 2 | 3 | 16640.3380 | -0.0002 |
| 3 | 3 | 0 | 3 | 2 | 1 | 16653.5852 | -0.0061 |
| 4 | 3 | 2 | 4 | 2 | 3 | 16658.3087 | -0.0005 |
| 5 | 3 | 3 | 5 | 2 | 4 | 16661.6831 | -0.0035 |
| 6 | 3 | 4 | 6 | 2 | 5 | 16667.6446 | 0.0025 |
| 9 | 0 | 9 | 8 | 1 | 8 | 17064.0736 | 0.0014 |
| 8 | 1 | 8 | 7 | 1 | 7 | 17225.1350 | -0.0015 |
| 8 | 0 | 8 | 7 | 0 | 7 | 17394.9151 | -0.0054 |
| 8 | 2 | 7 | 7 | 2 | 6 | 17438.2442 | 0.0007 |
| 8 | 4 | 4 | 7 | 4 | 3 | 17449.8616 | -0.0006 |
| 8 | 4 | 5 | 7 | 4 | 4 | 17449.8616 | -0.0006 |
| 8 | 3 | 6 | 7 | 3 | 5 | 17452.4759 | -0.0031 |
| 8 | 3 | 5 | 7 | 3 | 4 | 17453.6159 | 0.0001 |
| 8 | 2 | 6 | 7 | 2 | 5 | 17489.1502 | 0.0010 |
| 8 | 1 | 7 | 7 | 1 | 6 | 17641.8841 | -0.0029 |
| 7 | 1 | 7 | 6 | 0 | 6 | 17891.0777 | -0.0045 |

^aObserved frequency; ^bObserved-Calculated

Table S6. Full list of rotational transitions observed (in MHz) for the $^{13}\text{C}_5$ monosubstituted species of fluoroxene

| J' | K' ₋₁ | K' ₊₁ | J'' | K'' ₋₁ | K'' ₊₁ | obs. ^a | o.-c. ^b |
|----|------------------|------------------|-----|-------------------|-------------------|-------------------|--------------------|
| 3 | 1 | 3 | 2 | 1 | 2 | 6451.6177 | 0.0034 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6526.7651 | -0.0013 |
| 3 | 2 | 2 | 2 | 2 | 1 | 6529.1088 | -0.0042 |
| 3 | 2 | 1 | 2 | 2 | 0 | 6531.4843 | -0.0020 |
| 3 | 1 | 2 | 2 | 1 | 1 | 6605.9071 | -0.0023 |
| 2 | 1 | 2 | 1 | 0 | 1 | 7619.4274 | -0.0035 |
| 5 | 0 | 5 | 4 | 1 | 4 | 7776.0458 | 0.0012 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8601.4617 | -0.0010 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8699.5823 | -0.0006 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8705.0191 | 0.0045 |
| 4 | 3 | 1 | 3 | 3 | 0 | 8706.6260 | 0.0056 |
| 4 | 3 | 2 | 3 | 3 | 1 | 8706.6260 | 0.0056 |
| 4 | 2 | 2 | 3 | 2 | 1 | 8710.9427 | -0.0016 |
| 4 | 1 | 3 | 3 | 1 | 2 | 8807.1683 | -0.0007 |
| 10 | 2 | 8 | 10 | 1 | 9 | 8936.0578 | 0.0095 |
| 7 | 2 | 5 | 7 | 1 | 6 | 9393.7015 | -0.0051 |
| 3 | 1 | 3 | 2 | 0 | 2 | 9718.8750 | -0.0013 |
| 4 | 2 | 2 | 4 | 1 | 3 | 9784.2530 | -0.0006 |
| 3 | 2 | 1 | 3 | 1 | 2 | 9880.4592 | -0.0190 |
| 2 | 2 | 0 | 2 | 1 | 1 | 9954.9043 | 0.0029 |
| 6 | 0 | 6 | 5 | 1 | 5 | 10062.8572 | -0.0095 |
| 2 | 2 | 1 | 2 | 1 | 2 | 10108.6079 | 0.0000 |
| 3 | 2 | 2 | 3 | 1 | 3 | 10186.1084 | 0.0016 |
| 4 | 2 | 3 | 4 | 1 | 4 | 10289.6638 | 0.0052 |
| 5 | 2 | 4 | 5 | 1 | 5 | 10419.4420 | 0.0027 |
| 6 | 2 | 5 | 6 | 1 | 6 | 10575.6617 | 0.0086 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10750.7361 | 0.0029 |
| 7 | 2 | 6 | 7 | 1 | 7 | 10758.5144 | -0.0085 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10870.0370 | 0.0025 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10880.5088 | -0.0050 |
| 5 | 4 | 2 | 4 | 4 | 1 | 10883.0137 | -0.0094 |
| 5 | 4 | 1 | 4 | 4 | 0 | 10883.0137 | -0.0094 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10892.3605 | 0.0015 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11007.8098 | 0.0030 |
| 4 | 1 | 4 | 3 | 0 | 3 | 11793.5721 | -0.0006 |
| 7 | 0 | 7 | 6 | 1 | 6 | 12365.1883 | 0.0049 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12899.2887 | -0.0077 |
| 6 | 0 | 6 | 5 | 0 | 5 | 13037.5616 | 0.0063 |
| 6 | 2 | 5 | 5 | 2 | 4 | 13055.5062 | -0.0042 |
| 6 | 4 | 2 | 5 | 4 | 1 | 13060.0504 | 0.0055 |
| 6 | 4 | 3 | 5 | 4 | 2 | 13060.0504 | 0.0055 |
| 6 | 3 | 4 | 5 | 3 | 3 | 13061.2648 | 0.0024 |

| | | | | | | | |
|---|---|---|---|---|---|------------|---------|
| 6 | 3 | 3 | 5 | 3 | 2 | 13061.5117 | 0.0096 |
| 6 | 2 | 4 | 5 | 2 | 3 | 13076.2001 | 0.0065 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13207.6431 | -0.0081 |
| 5 | 1 | 5 | 4 | 0 | 4 | 13844.7231 | 0.0001 |
| 2 | 2 | 1 | 1 | 1 | 0 | 14358.4978 | -0.0012 |
| 2 | 2 | 0 | 1 | 1 | 1 | 14410.5269 | 0.0010 |
| 8 | 0 | 8 | 7 | 1 | 7 | 14679.8818 | 0.0012 |
| 7 | 1 | 7 | 6 | 1 | 6 | 15047.0335 | -0.0006 |
| 7 | 0 | 7 | 6 | 0 | 6 | 15201.6126 | -0.0005 |
| 7 | 2 | 6 | 6 | 2 | 5 | 15229.9034 | -0.0005 |
| 7 | 2 | 5 | 6 | 2 | 4 | 15262.8737 | -0.0041 |
| 7 | 1 | 6 | 6 | 1 | 5 | 15406.5199 | 0.0005 |
| 3 | 2 | 2 | 2 | 1 | 1 | 16483.4233 | 0.0023 |
| 3 | 2 | 1 | 2 | 1 | 2 | 16640.6954 | 0.0076 |
| 5 | 3 | 2 | 5 | 2 | 3 | 16703.6716 | 0.0007 |
| 4 | 3 | 1 | 4 | 2 | 2 | 16712.1629 | -0.0022 |
| 4 | 3 | 2 | 4 | 2 | 3 | 16721.0296 | -0.0022 |
| 6 | 3 | 4 | 6 | 2 | 5 | 16730.0458 | 0.0012 |
| 8 | 3 | 6 | 8 | 2 | 7 | 16753.0071 | -0.0012 |
| 9 | 0 | 9 | 8 | 1 | 8 | 17003.5568 | 0.0006 |
| 8 | 1 | 8 | 7 | 1 | 7 | 17193.8388 | -0.0009 |
| 8 | 0 | 8 | 7 | 0 | 7 | 17361.7321 | 0.0008 |
| 8 | 2 | 7 | 7 | 2 | 6 | 17403.5876 | -0.0072 |
| 8 | 4 | 4 | 7 | 4 | 3 | 17414.8094 | -0.0002 |
| 8 | 4 | 5 | 7 | 4 | 4 | 17414.8094 | -0.0002 |
| 8 | 3 | 6 | 7 | 3 | 5 | 17417.3553 | 0.0040 |
| 8 | 3 | 5 | 7 | 3 | 4 | 17418.4289 | 0.0006 |
| 8 | 2 | 6 | 7 | 2 | 5 | 17452.7842 | -0.0013 |
| 8 | 1 | 7 | 7 | 1 | 6 | 17604.2157 | 0.0003 |
| 7 | 1 | 7 | 6 | 0 | 6 | 17883.4649 | 0.0009 |

^aObserved frequency; ^bObserved-Calculated

Table S7. Cartesian coordinates (Å) of fluoroxene atoms for the different structural determinations

| | r_s^a | r_o | r_e |
|----------------------|---|-------------------------------|----------------------|
| | $a/b/c$ | $a/b/c$ | $a/b/c$ |
| C₁ | 3.1484(5) ^b /0.710(2)/[0.000] ^c | 3.152(2)/0.713(3)/[0.000] | 3.026/0.659/0.000 |
| C₂ | 2.4962(6)/-0.456(3)/[0.000] | 2.501(2)/-0.461(4)/[0.000] | 2.368/-0.512/0.000 |
| O₃ | 1.1454(13)/-0.654(2)/[0.000] | 1.151(3)/-0.655(3)/[0.000] | 1.020/-0.705/0.000 |
| C₄ | 0.316(5)/0.514(3)/[0.000] | 0.354(6)/0.519(3)/[0.000] | 0.249/0.472/0.000 |
| C₅ | -1.0746(14)/0.000(1)/[0.000] | -1.085(5)/0.068(8)/[0.000] | -1.205/0.060/0.000 |
| F₆ | | -1.878(6)/1.152(3)/ [0.000] | -1.974/1.167/0.000 |
| F₇ | | -1.390(6)/-0.650(3)/1.081(3) | -1.523/-0.660/1.083 |
| F₈ | | -1.390(6)/-0.650(3)/-1.081(3) | -1.523/-0.660/-1.083 |

^aSubstitution (r_s), effective (r_o) and *ab initio* (MP2/6-311++G(d,p)) equilibrium (r_e) structures ^b Standard errors in parentheses in units of the last digit. ^c Values in brackets were fixed in the fitting.











