

Table S-1 All the observed lines of the *gauche* form of isopropyl methyl sulfide.

| J | K- | K+ | --- | J | K- | K+ | Sym | obs/MHz | diff/MHz |
|---------------------------|----|----|-----|---|----|----|-----|-------------------------|----------|
| <i>a</i> -type transition | | | | | | | | | |
| 1 | 0 | 1 | --- | 0 | 0 | 0 | A | 4905.6714 | 0.0027 |
| 1 | 0 | 1 | --- | 0 | 0 | 0 | E | 4905.6583 | -0.0004 |
| 2 | 0 | 2 | --- | 1 | 0 | 1 | A | 9723.6956 | -0.0035 |
| 2 | 0 | 2 | --- | 1 | 0 | 1 | E | 9723.6808 | 0.0011 |
| 2 | 1 | 2 | --- | 1 | 1 | 1 | A | 9162.0255 | 0.0045 |
| 2 | 1 | 2 | --- | 1 | 1 | 1 | E | 9162.0073 | -0.0023 |
| 2 | 1 | 1 | --- | 1 | 1 | 0 | A | 10460.6065 | -0.0027 |
| 2 | 1 | 1 | --- | 1 | 1 | 0 | E | 10460.5833 | 0.0020 |
| 3 | 0 | 3 | --- | 2 | 0 | 2 | A | 14376.5514 | -0.0013 |
| 3 | 0 | 3 | --- | 2 | 0 | 2 | E | 14376.5256 | 0.0009 |
| 3 | 1 | 3 | --- | 2 | 1 | 2 | A | 13691.5016 | 0.0018 |
| 3 | 1 | 3 | --- | 2 | 1 | 2 | E | 13691.4793 | -0.0017 |
| 3 | 1 | 2 | --- | 2 | 1 | 1 | A | 15631.8828 | -0.0014 |
| 3 | 1 | 2 | --- | 2 | 1 | 1 | E | 15631.8463 | 0.0019 |
| 3 | 2 | 2 | --- | 2 | 2 | 1 | A | 14716.9098 | 0.0024 |
| 3 | 2 | 2 | --- | 2 | 2 | 1 | E | 14716.9285 | -0.0039 |
| 3 | 2 | 1 | --- | 2 | 2 | 0 | A | 15057.2941 | 0.0029 |
| 3 | 2 | 1 | --- | 2 | 2 | 0 | E | 15057.2079 | 0.0021 |
| 4 | 0 | 4 | --- | 3 | 0 | 3 | A | 18828.0821 | -0.0002 |
| 4 | 0 | 4 | --- | 3 | 0 | 3 | E | 18828.0474 | 0.0003 |
| 4 | 1 | 4 | --- | 3 | 1 | 3 | A | 18168.9236 | -0.0021 |
| 4 | 1 | 4 | --- | 3 | 1 | 3 | E | 18168.9026 | 0.0017 |
| 4 | 1 | 3 | --- | 3 | 1 | 2 | A | 20721.7378 | 0.0017 |
| 4 | 1 | 3 | --- | 3 | 1 | 2 | E | 20721.6834 | -0.0004 |
| 4 | 2 | 3 | --- | 3 | 2 | 2 | A | 19554.0287 | 0.0004 |
| 4 | 2 | 3 | --- | 3 | 2 | 2 | E | 19553.9983 | -0.0001 |
| 4 | 2 | 2 | --- | 3 | 2 | 1 | A | 20347.9182 | -0.0012 |
| 4 | 2 | 2 | --- | 3 | 2 | 1 | E | 20347.8682 | 0.0013 |
| 4 | 3 | 2 | --- | 3 | 3 | 1 | A | 19777.4335 ^a | -0.0003 |
| 4 | 3 | 2 | --- | 3 | 3 | 1 | E | 19778.6311 ^a | -0.0001 |
| 4 | 3 | 1 | --- | 3 | 3 | 0 | A | 19821.7144 | 0.0004 |

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|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 4 | 3 | 1 | --- | 3 | 3 | 0 | E | 19820.4397 ^a | 0.0025 |
| 4 | 2 | 3 | --- | 4 | 0 | 4 | A | 15500.1475 | -0.0007 |
| 4 | 2 | 3 | --- | 4 | 0 | 4 | E | 15499.9096 | 0.0006 |
| 5 | 0 | 5 | --- | 4 | 0 | 4 | A | 23114.5899 | -0.0003 |
| 5 | 0 | 5 | --- | 4 | 0 | 4 | E | 23114.5501 | 0.0004 |
| 5 | 1 | 5 | --- | 4 | 1 | 4 | A | 22591.1563 | -0.0014 |
| 5 | 1 | 5 | --- | 4 | 1 | 4 | E | 22591.1293 | 0.0015 |

b-type transition

| | | | | | | | | | |
|---|---|---|-----|---|---|---|---|------------|---------|
| 1 | 1 | 1 | --- | 0 | 0 | 0 | A | 8167.5829 | -0.0017 |
| 1 | 1 | 1 | --- | 0 | 0 | 0 | E | 8167.5173 | -0.0012 |
| 2 | 0 | 2 | --- | 1 | 1 | 1 | A | 6461.7789 | -0.0042 |
| 2 | 0 | 2 | --- | 1 | 1 | 1 | E | 6461.8242 | 0.0042 |
| 2 | 1 | 2 | --- | 1 | 0 | 1 | A | 12423.9340 | -0.0030 |
| 2 | 1 | 2 | --- | 1 | 0 | 1 | E | 12423.8678 | -0.0015 |
| 2 | 2 | 1 | --- | 1 | 1 | 0 | A | 20246.3311 | 0.0000 |
| 2 | 2 | 1 | --- | 1 | 1 | 0 | E | 20246.0715 | -0.0011 |
| 2 | 2 | 0 | --- | 1 | 1 | 1 | A | 20983.2511 | -0.0003 |
| 2 | 2 | 0 | --- | 1 | 1 | 1 | E | 20983.1254 | -0.0009 |
| 2 | 2 | 1 | --- | 2 | 1 | 2 | A | 11733.6090 | -0.0005 |
| 2 | 2 | 1 | --- | 2 | 1 | 2 | E | 11733.3593 | -0.0011 |
| 2 | 2 | 0 | --- | 2 | 1 | 1 | A | 9873.3405 | -0.0022 |
| 2 | 2 | 0 | --- | 2 | 1 | 1 | E | 9873.2470 | -0.0006 |
| 3 | 0 | 3 | --- | 2 | 1 | 2 | A | 11676.3129 | -0.0019 |
| 3 | 0 | 3 | --- | 2 | 1 | 2 | E | 11676.3349 | -0.0001 |
| 3 | 1 | 3 | --- | 2 | 0 | 2 | A | 16391.7305 | -0.0072 |
| 3 | 1 | 3 | --- | 2 | 0 | 2 | E | 16391.6759 | 0.0052 |
| 3 | 1 | 2 | --- | 2 | 2 | 1 | A | 5846.1667 | 0.0043 |
| 3 | 1 | 2 | --- | 2 | 2 | 1 | E | 5846.3556 | 0.0025 |
| 3 | 1 | 2 | --- | 3 | 0 | 3 | A | 5903.4593 | 0.0022 |
| 3 | 1 | 2 | --- | 3 | 0 | 3 | E | 5903.3770 | -0.0015 |
| 3 | 2 | 2 | --- | 3 | 1 | 3 | A | 12759.0147 | -0.0025 |
| 3 | 2 | 2 | --- | 3 | 1 | 3 | E | 12758.8112 | -0.0005 |
| 3 | 2 | 1 | --- | 3 | 1 | 2 | A | 9298.7471 | -0.0026 |
| 3 | 2 | 1 | --- | 3 | 1 | 2 | E | 9298.6089 | 0.0000 |

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|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 3 | 3 | 1 | --- | 3 | 2 | 2 | A | 17984.1862 ^a | 0.0009 |
| 3 | 3 | 1 | --- | 3 | 2 | 2 | E | 17982.4242 ^a | 0.0029 |
| 3 | 3 | 0 | --- | 3 | 2 | 1 | A | 17563.6533 ^a | 0.0015 |
| 3 | 3 | 0 | --- | 3 | 2 | 1 | E | 17564.8488 ^a | 0.0032 |
| 4 | 0 | 4 | --- | 3 | 1 | 3 | A | 16812.8981 | 0.0008 |
| 4 | 0 | 4 | --- | 3 | 1 | 3 | E | 16812.8981 | -0.0030 |
| 4 | 1 | 4 | --- | 3 | 0 | 3 | A | 20184.1104 | -0.0003 |
| 4 | 1 | 4 | --- | 3 | 0 | 3 | E | 20184.0470 | 0.0001 |
| 4 | 1 | 3 | --- | 3 | 2 | 2 | A | 11850.9883 | -0.0028 |
| 4 | 1 | 3 | --- | 3 | 2 | 2 | E | 11851.1051 | 0.0005 |
| 4 | 1 | 3 | --- | 4 | 0 | 4 | A | 7797.1122 | 0.0012 |
| 4 | 1 | 3 | --- | 4 | 0 | 4 | E | 7797.0154 | 0.0002 |
| 4 | 2 | 3 | --- | 4 | 1 | 4 | A | 14144.1200 | 0.0002 |
| 4 | 2 | 3 | --- | 4 | 1 | 4 | E | 14143.9082 | -0.0010 |
| 4 | 2 | 2 | --- | 4 | 1 | 3 | A | 8924.9333 | 0.0003 |
| 4 | 2 | 2 | --- | 4 | 1 | 3 | E | 8924.7918 | -0.0002 |
| 4 | 3 | 2 | --- | 4 | 2 | 3 | A | 18207.5894 | -0.0014 |
| 4 | 3 | 2 | --- | 4 | 2 | 3 | E | 18207.0565 | 0.0024 |
| 4 | 3 | 1 | --- | 4 | 2 | 2 | A | 17037.4424 | -0.0040 |
| 4 | 3 | 1 | --- | 4 | 2 | 2 | E | 17037.4218 | 0.0059 |
| 5 | 0 | 5 | --- | 4 | 1 | 4 | A | 21758.5653 | 0.0035 |
| 5 | 0 | 5 | --- | 4 | 1 | 4 | E | 21758.5473 | -0.0026 |
| 5 | 1 | 5 | --- | 4 | 0 | 4 | A | 23947.1848 | -0.0013 |
| 5 | 1 | 5 | --- | 4 | 0 | 4 | E | 23947.1294 | 0.0019 |
| 5 | 1 | 5 | --- | 4 | 2 | 2 | A | 7225.1398 | -0.0023 |
| 5 | 1 | 5 | --- | 4 | 2 | 2 | E | 7225.3208 | 0.0005 |
| 5 | 1 | 4 | --- | 4 | 2 | 3 | A | 17983.4370 | -0.0024 |
| 5 | 1 | 4 | --- | 4 | 2 | 3 | E | 17983.5208 | 0.0025 |
| 5 | 2 | 4 | --- | 4 | 3 | 1 | A | 6074.2752 | 0.0044 |
| 5 | 2 | 4 | --- | 4 | 3 | 1 | E | 6074.2486 | -0.0048 |
| 5 | 2 | 3 | --- | 4 | 3 | 2 | A | 8757.1373 | 0.0001 |
| 5 | 2 | 3 | --- | 4 | 3 | 2 | E | 8757.6166 | 0.0004 |
| 5 | 1 | 4 | --- | 5 | 0 | 5 | A | 10368.9987 | 0.0013 |
| 5 | 1 | 4 | --- | 5 | 0 | 5 | E | 10368.8769 | -0.0007 |
| 5 | 2 | 4 | --- | 5 | 1 | 5 | A | 15886.5753 | 0.0003 |

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|---|---|---|-----|---|---|---|---|------------|---------|
| 5 | 2 | 4 | --- | 5 | 1 | 5 | E | 15886.3491 | 0.0002 |
| 5 | 2 | 3 | --- | 5 | 1 | 4 | A | 8981.2894 | 0.0009 |
| 5 | 2 | 3 | --- | 5 | 1 | 4 | E | 8981.1519 | 0.0000 |
| 5 | 3 | 3 | --- | 5 | 2 | 4 | A | 18632.7939 | 0.0007 |
| 5 | 3 | 3 | --- | 5 | 2 | 4 | E | 18632.4424 | 0.0001 |
| 5 | 3 | 2 | --- | 5 | 2 | 3 | A | 16204.3611 | 0.0011 |
| 5 | 3 | 2 | --- | 5 | 2 | 3 | E | 16204.1489 | -0.0004 |
| 6 | 1 | 6 | --- | 5 | 2 | 3 | A | 8445.1422 | -0.0004 |
| 6 | 1 | 6 | --- | 5 | 2 | 3 | E | 8445.3465 | -0.0004 |
| 6 | 2 | 5 | --- | 5 | 3 | 2 | A | 10208.6916 | 0.0012 |
| 6 | 2 | 5 | --- | 5 | 3 | 2 | E | 10208.8582 | 0.0008 |
| 6 | 2 | 4 | --- | 5 | 3 | 3 | A | 15137.6909 | -0.0009 |
| 6 | 2 | 4 | --- | 5 | 3 | 3 | E | 15137.9560 | -0.0004 |
| 6 | 1 | 5 | --- | 6 | 0 | 6 | A | 13524.5770 | -0.0012 |
| 6 | 1 | 5 | --- | 6 | 0 | 6 | E | 13524.4279 | 0.0009 |
| 6 | 2 | 5 | --- | 6 | 1 | 6 | A | 17967.9086 | 0.0008 |
| 6 | 2 | 5 | --- | 6 | 1 | 6 | E | 17967.6600 | 0.0001 |
| 6 | 2 | 4 | --- | 6 | 1 | 5 | A | 9645.4519 | 0.0009 |
| 6 | 2 | 4 | --- | 6 | 1 | 5 | E | 9645.3165 | 0.0002 |
| 6 | 3 | 4 | --- | 6 | 2 | 5 | A | 19324.1170 | 0.0011 |
| 6 | 3 | 4 | --- | 6 | 2 | 5 | E | 19323.8028 | -0.0001 |
| 6 | 3 | 3 | --- | 6 | 2 | 4 | A | 15183.1913 | 0.0005 |
| 6 | 3 | 3 | --- | 6 | 2 | 4 | E | 15182.9512 | 0.0002 |
| 7 | 1 | 7 | --- | 6 | 2 | 4 | A | 8599.4056 | -0.0030 |
| 7 | 1 | 7 | --- | 6 | 2 | 4 | E | 8599.6531 | 0.0021 |
| 7 | 2 | 6 | --- | 6 | 3 | 3 | A | 13768.3845 | -0.0009 |
| 7 | 2 | 6 | --- | 6 | 3 | 3 | E | 13768.5921 | 0.0011 |
| 7 | 2 | 5 | --- | 6 | 3 | 4 | A | 21846.9524 | -0.0021 |
| 7 | 2 | 5 | --- | 6 | 3 | 4 | E | 21847.1489 | 0.0015 |
| 7 | 3 | 5 | --- | 6 | 4 | 2 | A | 9743.0544 | -0.0014 |
| 7 | 3 | 4 | --- | 6 | 4 | 3 | A | 11141.2160 | -0.0016 |
| 7 | 1 | 6 | --- | 7 | 0 | 7 | A | 17060.0071 | -0.0009 |
| 7 | 1 | 6 | --- | 7 | 0 | 7 | E | 17059.8210 | 0.0012 |
| 7 | 2 | 6 | --- | 7 | 1 | 7 | A | 20352.1684 | 0.0008 |
| 7 | 2 | 6 | --- | 7 | 1 | 7 | E | 20351.8915 | 0.0005 |

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| 7 | 2 | 5 | --- | 7 | 1 | 6 | A | 11043.3751 | 0.0011 |
| 7 | 2 | 5 | --- | 7 | 1 | 6 | E | 11043.2365 | 0.0007 |
| 7 | 3 | 5 | --- | 7 | 2 | 6 | A | 20333.1485 | 0.0009 |
| 7 | 3 | 5 | --- | 7 | 2 | 6 | E | 20332.8418 | 0.0010 |
| 7 | 3 | 4 | --- | 7 | 2 | 5 | A | 14214.8519 | 0.0004 |
| 7 | 3 | 4 | --- | 7 | 2 | 5 | E | 14214.6159 | -0.0005 |
| 7 | 4 | 3 | --- | 7 | 3 | 4 | A | 23694.5346 | -0.0009 |
| 7 | 4 | 3 | --- | 7 | 3 | 4 | E | 23694.4079 | 0.0024 |
| 8 | 2 | 7 | --- | 7 | 3 | 4 | A | 16524.2983 | -0.0002 |
| 8 | 2 | 7 | --- | 7 | 3 | 4 | E | 16524.5159 | -0.0008 |
| 8 | 3 | 6 | --- | 7 | 4 | 3 | A | 14522.1952 | 0.0018 |
| 8 | 3 | 6 | --- | 7 | 4 | 3 | E | 14522.2281 | -0.0017 |
| 8 | 3 | 5 | --- | 7 | 4 | 4 | A | 17360.1343 | -0.0006 |
| 8 | 3 | 5 | --- | 7 | 4 | 4 | E | 17360.7160 | -0.0006 |
| 8 | 4 | 5 | --- | 7 | 5 | 2 | A | 7867.9415 | -0.0003 |
| 8 | 4 | 4 | --- | 7 | 5 | 3 | A | 8113.7759 | 0.0030 |
| 8 | 1 | 7 | --- | 8 | 0 | 8 | A | 20743.7006 | -0.0015 |
| 8 | 1 | 7 | --- | 8 | 0 | 8 | E | 20743.4770 | -0.0002 |
| 8 | 2 | 7 | --- | 8 | 1 | 8 | A | 22989.6780 | -0.0006 |
| 8 | 2 | 7 | --- | 8 | 1 | 8 | E | 22989.3645 | 0.0008 |
| 8 | 2 | 6 | --- | 8 | 1 | 7 | A | 13239.6231 | -0.0001 |
| 8 | 2 | 6 | --- | 8 | 1 | 7 | E | 13239.4751 | 0.0012 |
| 8 | 3 | 6 | --- | 8 | 2 | 7 | A | 21692.4311 | 0.0007 |
| 8 | 3 | 6 | --- | 8 | 2 | 7 | E | 21692.1185 | -0.0001 |
| 8 | 3 | 5 | --- | 8 | 2 | 6 | A | 13587.7737 | 0.0003 |
| 8 | 3 | 5 | --- | 8 | 2 | 6 | E | 13587.5530 | -0.0002 |
| 8 | 4 | 4 | --- | 8 | 3 | 5 | A | 22679.4888 | 0.0005 |
| 8 | 4 | 4 | --- | 8 | 3 | 5 | E | 22679.1886 | -0.0011 |
| 9 | 2 | 8 | --- | 8 | 3 | 5 | A | 18264.4718 | -0.0012 |
| 9 | 2 | 8 | --- | 8 | 3 | 5 | E | 18264.7033 | 0.0007 |
| 9 | 3 | 7 | --- | 8 | 4 | 4 | A | 18996.7389 | -0.0002 |
| 9 | 3 | 7 | --- | 8 | 4 | 4 | E | 18996.9446 | 0.0007 |
| 9 | 2 | 7 | --- | 9 | 1 | 8 | A | 16194.2154 | -0.0005 |
| 9 | 2 | 7 | --- | 9 | 1 | 8 | E | 16194.0461 | 0.0004 |
| 9 | 3 | 7 | --- | 9 | 2 | 8 | A | 23411.7543 | -0.0001 |

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|---------------------------|---|---|-----|----|---|---|---|------------|---------|
| 9 | 3 | 7 | --- | 9 | 2 | 8 | E | 23411.4313 | 0.0003 |
| 9 | 3 | 6 | --- | 9 | 2 | 7 | A | 13559.1945 | 0.0004 |
| 9 | 3 | 6 | --- | 9 | 2 | 7 | E | 13558.9904 | 0.0000 |
| 9 | 4 | 5 | --- | 9 | 3 | 6 | A | 21359.4198 | 0.0000 |
| 9 | 4 | 5 | --- | 9 | 3 | 6 | E | 21359.0779 | -0.0022 |
| 10 | 3 | 8 | --- | 9 | 4 | 5 | A | 22979.7884 | -0.0007 |
| 10 | 3 | 8 | --- | 9 | 4 | 5 | E | 22980.0383 | 0.0013 |
| 10 | 4 | 7 | --- | 9 | 5 | 4 | A | 18166.6825 | -0.0002 |
| 10 | 4 | 7 | --- | 9 | 5 | 4 | E | 18166.0178 | 0.0038 |
| 10 | 2 | 8 | --- | 10 | 1 | 9 | A | 19739.5291 | -0.0018 |
| 10 | 2 | 8 | --- | 10 | 1 | 9 | E | 19739.3281 | -0.0008 |
| 10 | 3 | 7 | --- | 10 | 2 | 8 | A | 14314.4183 | 0.0005 |
| 10 | 3 | 7 | --- | 10 | 2 | 8 | E | 14314.2278 | 0.0010 |
| 10 | 4 | 6 | --- | 10 | 3 | 7 | A | 19922.7810 | -0.0005 |
| 10 | 4 | 6 | --- | 10 | 3 | 7 | E | 19922.4409 | -0.0023 |
| 11 | 3 | 8 | --- | 11 | 2 | 9 | A | 15961.6774 | -0.0001 |
| 11 | 3 | 8 | --- | 11 | 2 | 9 | E | 15961.4926 | 0.0004 |
| <i>c</i> -type transition | | | | | | | | | |
| 1 | 1 | 0 | --- | 0 | 0 | 0 | A | 8816.8813 | -0.0028 |
| 1 | 1 | 0 | --- | 0 | 0 | 0 | E | 8816.8163 | 0.0004 |
| 2 | 0 | 2 | --- | 1 | 1 | 0 | A | 5812.4897 | 0.0060 |
| 2 | 0 | 2 | --- | 1 | 1 | 0 | E | 5812.5206 | -0.0020 |
| 2 | 1 | 1 | --- | 1 | 0 | 1 | A | 14371.8255 | 0.0008 |
| 2 | 1 | 1 | --- | 1 | 0 | 1 | E | 14371.7393 | 0.0009 |
| 2 | 2 | 1 | --- | 1 | 1 | 1 | A | 20895.6285 | -0.0021 |
| 2 | 2 | 1 | --- | 1 | 1 | 1 | E | 20895.3698 | -0.0002 |
| 2 | 2 | 0 | --- | 1 | 1 | 0 | A | 20333.9514 | -0.0006 |
| 2 | 2 | 0 | --- | 1 | 1 | 0 | E | 20333.8294 | 0.0005 |
| 2 | 2 | 1 | --- | 2 | 1 | 1 | A | 9785.7192 | -0.0026 |
| 2 | 2 | 1 | --- | 2 | 1 | 1 | E | 9785.4909 | -0.0004 |
| 2 | 2 | 0 | --- | 2 | 1 | 2 | A | 11821.2274 | -0.0030 |
| 2 | 2 | 0 | --- | 2 | 1 | 2 | E | 11821.1170 | 0.0003 |
| 3 | 0 | 3 | --- | 2 | 1 | 1 | A | 9728.4311 | 0.0040 |
| 3 | 0 | 3 | --- | 2 | 1 | 1 | E | 9728.4655 | -0.0004 |
| 3 | 1 | 2 | --- | 2 | 0 | 2 | A | 20280.0091 | -0.0007 |

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|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 3 | 1 | 2 | --- | 2 | 0 | 2 | E | 20279.9041 | 0.0010 |
| 3 | 1 | 2 | --- | 2 | 2 | 0 | A | 5758.5511 | 0.0096 |
| 3 | 1 | 2 | --- | 2 | 2 | 0 | E | 5758.5973 | 0.0005 |
| 3 | 2 | 2 | --- | 3 | 1 | 2 | A | 8870.7447 | -0.0004 |
| 3 | 2 | 2 | --- | 3 | 1 | 2 | E | 8870.5772 | -0.0020 |
| 3 | 2 | 1 | --- | 3 | 1 | 3 | A | 13187.0176 | -0.0042 |
| 3 | 2 | 1 | --- | 3 | 1 | 3 | E | 13186.8421 | 0.0007 |
| 3 | 3 | 1 | --- | 3 | 2 | 1 | A | 17556.1826 ^a | 0.0020 |
| 3 | 3 | 1 | --- | 3 | 2 | 1 | E | 17554.3941 ^a | 0.0025 |
| 3 | 3 | 0 | --- | 3 | 2 | 2 | A | 17991.6578 ^a | 0.0013 |
| 3 | 3 | 0 | --- | 3 | 2 | 2 | E | 17992.8800 ^a | 0.0047 |
| 4 | 0 | 4 | --- | 3 | 1 | 2 | A | 12924.6228 | -0.0024 |
| 4 | 0 | 4 | --- | 3 | 1 | 2 | E | 12924.6689 | 0.0002 |
| 4 | 1 | 3 | --- | 3 | 2 | 1 | A | 11422.9873 | 0.0009 |
| 4 | 1 | 3 | --- | 3 | 2 | 1 | E | 11423.0743 | -0.0006 |
| 4 | 2 | 3 | --- | 4 | 1 | 3 | A | 7703.0374 | 0.0002 |
| 4 | 2 | 3 | --- | 4 | 1 | 3 | E | 7702.8907 | -0.0031 |
| 4 | 2 | 2 | --- | 4 | 1 | 4 | A | 15366.0127 | -0.0029 |
| 4 | 2 | 2 | --- | 4 | 1 | 4 | E | 15365.8091 | 0.0017 |
| 4 | 3 | 2 | --- | 4 | 2 | 2 | A | 16985.6941 | -0.0009 |
| 4 | 3 | 2 | --- | 4 | 2 | 2 | E | 16985.1535 | -0.0024 |
| 4 | 3 | 1 | --- | 4 | 2 | 3 | A | 18259.3373 | -0.0049 |
| 4 | 3 | 1 | --- | 4 | 2 | 3 | E | 18259.3203 | 0.0062 |
| 5 | 0 | 5 | --- | 4 | 1 | 3 | A | 15317.4798 | 0.0006 |
| 5 | 0 | 5 | --- | 4 | 1 | 3 | E | 15317.5338 | -0.0007 |
| 5 | 1 | 5 | --- | 4 | 2 | 3 | A | 8447.0366 | -0.0013 |
| 5 | 1 | 5 | --- | 4 | 2 | 3 | E | 8447.2194 | 0.0009 |
| 5 | 1 | 4 | --- | 4 | 2 | 2 | A | 16761.5416 | -0.0020 |
| 5 | 1 | 4 | --- | 4 | 2 | 2 | E | 16761.6225 | 0.0024 |
| 5 | 2 | 4 | --- | 5 | 1 | 4 | A | 6350.1737 | 0.0002 |
| 5 | 2 | 4 | --- | 5 | 1 | 4 | E | 6350.0495 | 0.0004 |
| 5 | 2 | 3 | --- | 5 | 1 | 5 | A | 18517.6890 | -0.0010 |
| 5 | 2 | 3 | --- | 5 | 1 | 5 | E | 18517.4506 | -0.0011 |
| 5 | 3 | 3 | --- | 5 | 2 | 3 | A | 16001.6783 | 0.0002 |
| 5 | 3 | 3 | --- | 5 | 2 | 3 | E | 16001.3395 | 0.0000 |

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|---|---|---|-----|---|---|---|---|------------|---------|
| 5 | 3 | 2 | --- | 5 | 2 | 4 | A | 18835.4751 | 0.0000 |
| 5 | 3 | 2 | --- | 5 | 2 | 4 | E | 18835.2528 | 0.0007 |
| 6 | 0 | 6 | --- | 5 | 1 | 4 | A | 16950.6249 | -0.0044 |
| 6 | 0 | 6 | --- | 5 | 1 | 4 | E | 16950.7078 | 0.0033 |
| 6 | 1 | 6 | --- | 5 | 2 | 4 | A | 11076.2580 | 0.0004 |
| 6 | 1 | 6 | --- | 5 | 2 | 4 | E | 11076.4505 | 0.0008 |
| 6 | 1 | 5 | --- | 5 | 2 | 3 | A | 21493.9195 | 0.0006 |
| 6 | 1 | 5 | --- | 5 | 2 | 3 | E | 21493.9793 | -0.0003 |
| 6 | 2 | 5 | --- | 5 | 3 | 3 | A | 10411.3727 | 0.0005 |
| 6 | 2 | 5 | --- | 5 | 3 | 3 | E | 10411.6681 | 0.0008 |
| 6 | 2 | 4 | --- | 5 | 3 | 2 | A | 14935.0096 | -0.0004 |
| 6 | 2 | 4 | --- | 5 | 3 | 2 | E | 14935.1469 | 0.0003 |
| 6 | 2 | 5 | --- | 6 | 1 | 5 | A | 4919.1320 | 0.0006 |
| 6 | 2 | 5 | --- | 6 | 1 | 5 | E | 4919.0264 | -0.0008 |
| 6 | 2 | 4 | --- | 6 | 1 | 6 | A | 22694.2218 | -0.0056 |
| 6 | 2 | 4 | --- | 6 | 1 | 6 | E | 22693.9489 | -0.0001 |
| 6 | 3 | 4 | --- | 6 | 2 | 4 | A | 14597.7967 | 0.0004 |
| 6 | 3 | 4 | --- | 6 | 2 | 4 | E | 14597.5143 | 0.0006 |
| 7 | 0 | 7 | --- | 6 | 1 | 5 | A | 17986.8180 | -0.0019 |
| 7 | 0 | 7 | --- | 6 | 1 | 5 | E | 17986.9230 | 0.0012 |
| 7 | 1 | 7 | --- | 6 | 2 | 5 | A | 13325.7286 | 0.0004 |
| 7 | 1 | 7 | --- | 6 | 2 | 5 | E | 13325.9405 | 0.0004 |
| 7 | 2 | 6 | --- | 6 | 3 | 4 | A | 14353.7794 | -0.0005 |
| 7 | 2 | 6 | --- | 6 | 3 | 4 | E | 14354.0284 | 0.0001 |
| 7 | 2 | 5 | --- | 6 | 3 | 3 | A | 21261.5581 | -0.0019 |
| 7 | 2 | 5 | --- | 6 | 3 | 3 | E | 21261.7106 | 0.0005 |
| 7 | 3 | 5 | --- | 6 | 4 | 3 | A | 9766.3392 | 0.0000 |
| 7 | 3 | 5 | --- | 6 | 4 | 3 | E | 9767.6104 | 0.0007 |
| 7 | 3 | 4 | --- | 6 | 4 | 2 | A | 11117.9315 | -0.0027 |
| 7 | 3 | 5 | --- | 7 | 2 | 5 | A | 12839.9735 | 0.0004 |
| 7 | 3 | 5 | --- | 7 | 2 | 5 | E | 12839.7215 | -0.0002 |
| 7 | 3 | 4 | --- | 7 | 2 | 6 | A | 21708.0273 | 0.0012 |
| 7 | 3 | 4 | --- | 7 | 2 | 6 | E | 21707.7359 | 0.0004 |
| 7 | 4 | 4 | --- | 7 | 3 | 4 | A | 23610.8228 | 0.0002 |
| 7 | 4 | 4 | --- | 7 | 3 | 4 | E | 23610.1520 | 0.0015 |

| | | | | | | | | | |
|---|---|---|-----|---|---|---|---|------------|---------|
| 8 | 0 | 8 | --- | 7 | 1 | 6 | A | 18658.0840 | -0.0004 |
| 8 | 0 | 8 | --- | 7 | 1 | 6 | E | 18658.2168 | 0.0018 |
| 8 | 1 | 8 | --- | 7 | 2 | 6 | A | 15242.6446 | -0.0014 |
| 8 | 1 | 8 | --- | 7 | 2 | 6 | E | 15242.8865 | -0.0020 |
| 8 | 2 | 7 | --- | 7 | 3 | 5 | A | 17899.1760 | -0.0010 |
| 8 | 2 | 7 | --- | 7 | 3 | 5 | E | 17899.4118 | 0.0003 |
| 8 | 3 | 6 | --- | 7 | 4 | 4 | A | 14605.9065 | 0.0002 |
| 8 | 3 | 6 | --- | 7 | 4 | 4 | E | 14606.4843 | -0.0005 |
| 8 | 3 | 5 | --- | 7 | 4 | 3 | A | 17276.4221 | 0.0001 |
| 8 | 3 | 5 | --- | 7 | 4 | 3 | E | 17276.4594 | -0.0022 |
| 8 | 4 | 5 | --- | 7 | 5 | 3 | A | 7870.1303 | 0.0001 |
| 8 | 3 | 6 | --- | 8 | 2 | 6 | A | 10833.5455 | 0.0007 |
| 8 | 3 | 6 | --- | 8 | 2 | 6 | E | 10833.3202 | -0.0012 |

^a Averaged value.

Table S-2 All the observed lines of the *trans* form of isopropyl methyl sulfide.

| J | K- | K+ | --- | J | K- | K+ | Sym | obs/MHz | diff/MHz |
|---------------------------|----|----|-----|---|----|----|-----|------------|----------|
| <i>a</i> -type transition | | | | | | | | | |
| 1 | 0 | 1 | --- | 0 | 0 | 0 | A | 5352.8605 | 0.0018 |
| 1 | 0 | 1 | --- | 0 | 0 | 0 | E | 5352.8303 | -0.0004 |
| 2 | 0 | 2 | --- | 1 | 0 | 1 | A | 10693.8430 | 0.0005 |
| 2 | 0 | 2 | --- | 1 | 0 | 1 | E | 10693.7828 | -0.0001 |
| 2 | 1 | 2 | --- | 1 | 1 | 1 | A | 10509.6962 | 0.0031 |
| 2 | 1 | 2 | --- | 1 | 1 | 1 | E | 10509.6162 | 0.0026 |
| 2 | 1 | 1 | --- | 1 | 1 | 0 | A | 10901.6460 | -0.0019 |
| 2 | 1 | 1 | --- | 1 | 1 | 0 | E | 10901.6203 | 0.0023 |
| 3 | 0 | 3 | --- | 2 | 0 | 2 | A | 16011.3603 | -0.0014 |
| 3 | 0 | 3 | --- | 2 | 0 | 2 | E | 16011.2650 | 0.0014 |
| 3 | 1 | 3 | --- | 2 | 1 | 2 | A | 15757.2721 | -0.0024 |
| 3 | 1 | 3 | --- | 2 | 1 | 2 | E | 15757.1509 | 0.0000 |
| 3 | 1 | 2 | --- | 2 | 1 | 1 | A | 16344.7522 | -0.0021 |
| 3 | 1 | 2 | --- | 2 | 1 | 1 | E | 16344.7137 | 0.0038 |
| 3 | 2 | 2 | --- | 2 | 2 | 1 | A | 16058.3228 | -0.0037 |
| 3 | 2 | 2 | --- | 2 | 2 | 1 | E | 16058.4117 | -0.0054 |
| 3 | 2 | 1 | --- | 2 | 2 | 0 | A | 16105.4747 | -0.0029 |
| 3 | 2 | 1 | --- | 2 | 2 | 0 | E | 16105.2352 | 0.0003 |
| 4 | 0 | 4 | --- | 3 | 0 | 3 | A | 21295.2060 | -0.0008 |
| 4 | 0 | 4 | --- | 3 | 0 | 3 | E | 21295.0609 | 0.0003 |
| 4 | 1 | 4 | --- | 3 | 1 | 3 | A | 20996.7501 | -0.0022 |
| 4 | 1 | 4 | --- | 3 | 1 | 3 | E | 20996.5859 | 0.0008 |
| 4 | 1 | 3 | --- | 3 | 1 | 2 | A | 21777.9587 | -0.0005 |
| 4 | 1 | 3 | --- | 3 | 1 | 2 | E | 21777.8990 | 0.0029 |
| 4 | 2 | 3 | --- | 3 | 2 | 2 | A | 21401.7059 | -0.0010 |
| 4 | 2 | 3 | --- | 3 | 2 | 2 | E | 21401.6244 | 0.0006 |
| 4 | 2 | 2 | --- | 3 | 2 | 1 | A | 21517.7598 | -0.0024 |
| 4 | 2 | 2 | --- | 3 | 2 | 1 | E | 21517.6554 | 0.0034 |
| 4 | 3 | 2 | --- | 3 | 3 | 1 | A | 21433.2262 | -0.0014 |
| 4 | 3 | 2 | --- | 3 | 3 | 1 | E | 21434.0235 | 0.0004 |
| 4 | 3 | 1 | --- | 3 | 3 | 0 | A | 21435.9198 | -0.0049 |

| | | | | | | | | | |
|---------------------------|---|---|-----|---|---|---|---|------------|---------|
| 4 | 3 | 1 | --- | 3 | 3 | 0 | E | 21434.9231 | 0.0005 |
| <i>c</i> -type transition | | | | | | | | | |
| 1 | 1 | 0 | --- | 0 | 0 | 0 | A | 7879.8114 | -0.0002 |
| 1 | 1 | 0 | --- | 0 | 0 | 0 | E | 7879.7974 | -0.0002 |
| 2 | 0 | 2 | --- | 1 | 1 | 0 | A | 8166.8936 | 0.0039 |
| 2 | 0 | 2 | --- | 1 | 1 | 0 | E | 8166.8159 | -0.0001 |
| 2 | 1 | 1 | --- | 1 | 0 | 1 | A | 13428.6000 | -0.0008 |
| 2 | 1 | 1 | --- | 1 | 0 | 1 | E | 13428.5837 | -0.0012 |
| 2 | 2 | 0 | --- | 1 | 1 | 0 | A | 17906.4196 | -0.0010 |
| 2 | 2 | 0 | --- | 1 | 1 | 0 | E | 17906.5562 | -0.0022 |
| 2 | 2 | 1 | --- | 1 | 1 | 1 | A | 18090.5361 | -0.0032 |
| 2 | 2 | 1 | --- | 1 | 1 | 1 | E | 18090.2740 | 0.0010 |
| 2 | 2 | 1 | --- | 2 | 1 | 1 | A | 6992.9151 | 0.0015 |
| 2 | 2 | 1 | --- | 2 | 1 | 1 | E | 6992.6435 | 0.0000 |
| 2 | 2 | 0 | --- | 2 | 1 | 2 | A | 7592.6992 | -0.0060 |
| 2 | 2 | 0 | --- | 2 | 1 | 2 | E | 7592.9573 | 0.0009 |
| 3 | 0 | 3 | --- | 2 | 1 | 1 | A | 13276.6068 | 0.0034 |
| 3 | 0 | 3 | --- | 2 | 1 | 1 | E | 13276.4614 | -0.0003 |
| 3 | 1 | 2 | --- | 2 | 0 | 2 | A | 19079.5120 | -0.0006 |
| 3 | 1 | 2 | --- | 2 | 0 | 2 | E | 19079.5120 | 0.0001 |
| 3 | 1 | 3 | --- | 2 | 2 | 1 | A | 8176.4315 | 0.0032 |
| 3 | 1 | 3 | --- | 2 | 2 | 1 | E | 8176.4916 | 0.0001 |
| 3 | 1 | 2 | --- | 2 | 2 | 0 | A | 9339.9766 | -0.0051 |
| 3 | 1 | 2 | --- | 2 | 2 | 0 | E | 9339.7716 | 0.0021 |
| 3 | 2 | 1 | --- | 2 | 1 | 1 | A | 23110.2504 | 0.0002 |
| 3 | 2 | 1 | --- | 2 | 1 | 1 | E | 23110.1753 | -0.0001 |
| 3 | 2 | 2 | --- | 2 | 1 | 2 | A | 23639.1728 | 0.0002 |
| 3 | 2 | 2 | --- | 2 | 1 | 2 | E | 23639.0769 | 0.0003 |
| 3 | 2 | 2 | --- | 3 | 1 | 2 | A | 6706.4836 | -0.0021 |
| 3 | 2 | 2 | --- | 3 | 1 | 2 | E | 6706.3478 | -0.0028 |
| 3 | 2 | 1 | --- | 3 | 1 | 3 | A | 7940.9049 | -0.0033 |
| 3 | 2 | 1 | --- | 3 | 1 | 3 | E | 7941.0421 | 0.0017 |
| 3 | 3 | 1 | --- | 3 | 2 | 1 | A | 12093.0478 | -0.0056 |
| 3 | 3 | 1 | --- | 3 | 2 | 1 | E | 12090.7640 | 0.0014 |
| 3 | 3 | 0 | --- | 3 | 2 | 2 | A | 12152.5149 | 0.0008 |

| | | | | | | | | | |
|---|---|---|-----|---|---|---|---|------------|---------|
| 3 | 3 | 0 | --- | 3 | 2 | 2 | E | 12154.7563 | -0.0006 |
| 3 | 3 | 1 | --- | 3 | 2 | 2 | E | 12149.8819 | 0.0045 |
| 3 | 3 | 0 | --- | 3 | 2 | 1 | E | 12095.6429 | 0.0007 |
| 4 | 1 | 4 | --- | 3 | 2 | 2 | A | 13114.8573 | 0.0031 |
| 4 | 1 | 4 | --- | 3 | 2 | 2 | E | 13114.6581 | -0.0013 |
| 4 | 1 | 3 | --- | 3 | 2 | 1 | A | 15012.4633 | 0.0000 |
| 4 | 1 | 3 | --- | 3 | 2 | 1 | E | 15012.4368 | 0.0061 |
| 4 | 0 | 4 | --- | 3 | 1 | 2 | A | 18227.0585 | 0.0025 |
| 4 | 0 | 4 | --- | 3 | 1 | 2 | E | 18226.8120 | -0.0003 |
| 4 | 2 | 3 | --- | 4 | 1 | 3 | A | 6330.2298 | -0.0037 |
| 4 | 2 | 3 | --- | 4 | 1 | 3 | E | 6330.0765 | -0.0018 |
| 4 | 2 | 2 | --- | 4 | 1 | 4 | A | 8461.9129 | -0.0052 |
| 4 | 2 | 2 | --- | 4 | 1 | 4 | E | 8462.1099 | 0.0026 |
| 4 | 3 | 2 | --- | 4 | 2 | 2 | A | 12008.5226 | 0.0038 |
| 4 | 3 | 2 | --- | 4 | 2 | 2 | E | 12007.1343 | 0.0006 |
| 4 | 3 | 1 | --- | 4 | 2 | 3 | A | 12186.7359 | 0.0040 |
| 4 | 3 | 1 | --- | 4 | 2 | 3 | E | 12188.0630 | 0.0073 |
| 4 | 4 | 1 | --- | 4 | 3 | 1 | A | 16979.3372 | -0.0043 |
| 4 | 4 | 0 | --- | 4 | 3 | 2 | A | 16982.5095 | 0.0061 |
| 4 | 4 | 0 | --- | 4 | 3 | 2 | E | 16987.0190 | 0.0018 |
| 4 | 4 | 1 | --- | 4 | 3 | 2 | E | 16980.5453 | 0.0009 |
| 4 | 4 | 0 | --- | 4 | 3 | 1 | E | 16981.2392 | 0.0010 |
| 5 | 1 | 5 | --- | 4 | 2 | 3 | A | 17939.5523 | 0.0014 |
| 5 | 1 | 5 | --- | 4 | 2 | 3 | E | 17939.2261 | -0.0018 |
| 5 | 1 | 4 | --- | 4 | 2 | 2 | A | 20691.5808 | -0.0052 |
| 5 | 1 | 4 | --- | 4 | 2 | 2 | E | 20691.5808 | 0.0035 |
| 5 | 0 | 5 | --- | 4 | 1 | 3 | A | 22987.9446 | 0.0038 |
| 5 | 0 | 5 | --- | 4 | 1 | 3 | E | 22987.5538 | -0.0010 |
| 5 | 2 | 4 | --- | 5 | 1 | 4 | A | 5870.4146 | -0.0002 |
| 5 | 2 | 4 | --- | 5 | 1 | 4 | E | 5870.2068 | -0.0029 |
| 5 | 2 | 3 | --- | 5 | 1 | 5 | A | 9197.5946 | -0.0048 |
| 5 | 2 | 3 | --- | 5 | 1 | 5 | E | 9197.9101 | 0.0033 |
| 5 | 3 | 3 | --- | 5 | 2 | 3 | A | 11845.9349 | 0.0024 |
| 5 | 3 | 3 | --- | 5 | 2 | 3 | E | 11845.3783 | -0.0014 |
| 5 | 3 | 2 | --- | 5 | 2 | 4 | A | 12258.5619 | 0.0044 |

| | | | | | | | | | |
|---|---|---|-----|---|---|---|---|------------|---------|
| 5 | 3 | 2 | --- | 5 | 2 | 4 | E | 12259.0282 | 0.0014 |
| 5 | 4 | 2 | --- | 5 | 3 | 2 | A | 16959.7875 | 0.0029 |
| 5 | 4 | 2 | --- | 5 | 3 | 2 | E | 16956.1352 | 0.0006 |
| 5 | 4 | 1 | --- | 5 | 3 | 3 | A | 16972.4606 | 0.0072 |
| 5 | 4 | 1 | --- | 5 | 3 | 3 | E | 16976.0314 | -0.0017 |
| 5 | 4 | 2 | --- | 5 | 3 | 3 | E | 16969.5728 | -0.0043 |
| 5 | 4 | 1 | --- | 5 | 3 | 2 | E | 16962.5907 | 0.0000 |
| 5 | 5 | 1 | --- | 5 | 4 | 1 | A | 21836.4313 | -0.0082 |
| 5 | 5 | 0 | --- | 5 | 4 | 2 | A | 21836.5593 | -0.0086 |
| 5 | 5 | 1 | --- | 5 | 4 | 2 | E | 21835.6525 | 0.0008 |
| 5 | 5 | 0 | --- | 5 | 4 | 1 | E | 21837.2765 | -0.0011 |
| 6 | 2 | 4 | --- | 5 | 3 | 2 | A | 20577.9978 | -0.0026 |
| 6 | 1 | 6 | --- | 5 | 2 | 4 | A | 22647.7226 | 0.0012 |
| 6 | 1 | 6 | --- | 5 | 2 | 4 | E | 22647.2801 | 0.0002 |
| 6 | 2 | 4 | --- | 6 | 1 | 6 | A | 10188.8319 | -0.0046 |
| 6 | 2 | 4 | --- | 6 | 1 | 6 | E | 10189.3154 | 0.0047 |
| 6 | 2 | 5 | --- | 6 | 1 | 5 | A | 5336.6368 | -0.0026 |
| 6 | 2 | 5 | --- | 6 | 1 | 5 | E | 5336.3711 | -0.0031 |
| 6 | 3 | 4 | --- | 6 | 2 | 4 | A | 11578.3326 | 0.0022 |
| 6 | 3 | 4 | --- | 6 | 2 | 4 | E | 11578.0061 | -0.0028 |
| 6 | 3 | 3 | --- | 6 | 2 | 5 | A | 12389.7733 | 0.0050 |
| 6 | 3 | 3 | --- | 6 | 2 | 5 | E | 12389.9779 | -0.0001 |
| 6 | 4 | 3 | --- | 6 | 3 | 3 | A | 16921.5053 | 0.0035 |
| 6 | 4 | 3 | --- | 6 | 3 | 3 | E | 16918.3846 | -0.0016 |
| 6 | 4 | 2 | --- | 6 | 3 | 4 | A | 16959.5051 | 0.0044 |
| 6 | 4 | 2 | --- | 6 | 3 | 4 | E | 16962.5281 | -0.0039 |
| 6 | 4 | 2 | --- | 6 | 3 | 3 | E | 16924.8463 | -0.0032 |
| 6 | 5 | 2 | --- | 6 | 4 | 2 | A | 21825.0292 | 0.0045 |
| 6 | 5 | 1 | --- | 6 | 4 | 3 | A | 21825.6707 | 0.0027 |
| 6 | 5 | 2 | --- | 6 | 4 | 3 | E | 21824.5078 | 0.0001 |
| 6 | 5 | 1 | --- | 6 | 4 | 2 | E | 21826.1003 | -0.0010 |
| 7 | 2 | 6 | --- | 7 | 1 | 6 | A | 4742.9576 | -0.0009 |
| 7 | 2 | 6 | --- | 7 | 1 | 6 | E | 4742.6294 | -0.0024 |
| 7 | 2 | 5 | --- | 7 | 1 | 7 | E | 11468.0946 | -0.0017 |
| 7 | 3 | 5 | --- | 7 | 2 | 5 | A | 11186.7583 | -0.0003 |

| | | | | | | | | | |
|----|---|---|-----|----|---|---|---|------------|---------|
| 7 | 3 | 5 | --- | 7 | 2 | 5 | E | 11186.4384 | -0.0027 |
| 7 | 3 | 4 | --- | 7 | 2 | 6 | A | 12608.6495 | 0.0052 |
| 7 | 3 | 4 | --- | 7 | 2 | 6 | E | 12608.8249 | 0.0001 |
| 7 | 4 | 4 | --- | 7 | 3 | 4 | A | 16852.1996 | 0.0033 |
| 7 | 4 | 4 | --- | 7 | 3 | 4 | E | 16849.8211 | -0.0006 |
| 7 | 4 | 3 | --- | 7 | 3 | 5 | A | 16946.8791 | 0.0033 |
| 7 | 4 | 3 | --- | 7 | 3 | 5 | E | 16949.1519 | 0.0086 |
| 7 | 5 | 3 | --- | 7 | 4 | 3 | A | 21806.5866 | 0.0012 |
| 7 | 5 | 2 | --- | 7 | 4 | 4 | A | 21808.9538 | 0.0075 |
| 7 | 5 | 3 | --- | 7 | 4 | 4 | E | 21807.1096 | -0.0040 |
| 7 | 5 | 2 | --- | 7 | 4 | 3 | E | 21808.3171 | -0.0082 |
| 8 | 4 | 5 | --- | 8 | 3 | 5 | A | 16734.5266 | 0.0018 |
| 8 | 4 | 5 | --- | 8 | 3 | 5 | E | 16733.1491 | 0.0011 |
| 8 | 4 | 4 | --- | 8 | 3 | 6 | A | 16941.1435 | 0.0024 |
| 8 | 4 | 4 | --- | 8 | 3 | 6 | E | 16942.3829 | 0.0067 |
| 8 | 5 | 3 | --- | 8 | 4 | 5 | A | 21785.1191 | 0.0039 |
| 9 | 4 | 6 | --- | 9 | 3 | 6 | A | 16545.9584 | 0.0012 |
| 9 | 4 | 6 | --- | 9 | 3 | 6 | E | 16545.2239 | -0.0015 |
| 9 | 4 | 5 | --- | 9 | 3 | 7 | A | 16953.1520 | 0.0007 |
| 9 | 4 | 5 | --- | 9 | 3 | 7 | E | 16953.6858 | -0.0070 |
| 9 | 5 | 5 | --- | 9 | 4 | 5 | A | 21734.9931 | 0.0004 |
| 9 | 5 | 4 | --- | 9 | 4 | 6 | A | 21753.3588 | 0.0012 |
| 10 | 4 | 7 | --- | 10 | 3 | 7 | A | 16260.2334 | 0.0029 |
| 10 | 4 | 7 | --- | 10 | 3 | 7 | E | 16259.7124 | -0.0014 |
| 10 | 4 | 6 | --- | 10 | 3 | 8 | A | 16998.9664 | 0.0000 |
| 10 | 4 | 6 | --- | 10 | 3 | 8 | E | 16999.2225 | -0.0074 |
| 10 | 5 | 6 | --- | 10 | 4 | 6 | A | 21671.1428 | -0.0021 |
| 10 | 5 | 5 | --- | 10 | 4 | 7 | A | 21713.7933 | -0.0018 |

Table S-3 Molecular parameters and the observed transition frequencies of the *trans* form of isopropyl methyl sulfide (IPMS) in the satellite state, which is possibly the excited isopC-S torsional state.^d

| | | | |
|---------------|-----------------|------------|-------------------------------|
| A | 5105.39031 (35) | I_α | 3.139995 ^b |
| B | 2774.42434 (28) | θ_a | 111.816 ^{o a,b} |
| C | 2578.42095 (26) | θ_b | 90.00 ^{o a,b} |
| Δ_J | 0.0012547 (59) | θ_c | 21.816 ^{o a,b} |
| Δ_{JK} | 0.0041863 (40) | F_0 | 160949. ^b |
| Δ_K | -0.0037438 (87) | V_3 | 559.413 (38) cm ⁻¹ |
| δ_J | -0.0000230 (18) | s | 45.4685 (31) |
| δ_K | 0.00029933 (53) | σ^c | 0.0076 |

| J | K- | K+ | --- | J | K- | K+ | Sym | obs/MHz | diff/MHz |
|---------------------------|----|----|-----|---|----|----|-----|-------------------------|----------|
| <i>a</i> -type transition | | | | | | | | | |
| 1 | 0 | 1 | --- | 0 | 0 | 0 | A | 5352.8463 | -0.0123 |
| 1 | 0 | 1 | --- | 0 | 0 | 0 | E | 5352.8303 ^e | -0.0004 |
| 2 | 0 | 2 | --- | 1 | 0 | 1 | A | 10693.8430 ^e | 0.0009 |
| 2 | 0 | 2 | --- | 1 | 0 | 1 | E | 10693.7828 ^e | 0.0000 |
| 2 | 1 | 2 | --- | 1 | 1 | 1 | A | 10509.6962 ^e | 0.0052 |
| 2 | 1 | 2 | --- | 1 | 1 | 1 | E | 10509.6162 ^e | 0.0044 |
| 2 | 1 | 1 | --- | 1 | 1 | 0 | A | 10901.6343 | -0.0153 |
| 2 | 1 | 1 | --- | 1 | 1 | 0 | E | 10901.6203 ^e | 0.0006 |
| 3 | 0 | 3 | --- | 2 | 0 | 2 | A | 16011.3603 ^e | -0.0005 |
| 3 | 0 | 3 | --- | 2 | 0 | 2 | E | 16011.2650 ^e | 0.0019 |
| 3 | 1 | 3 | --- | 2 | 1 | 2 | A | 15757.2721 ^e | 0.0003 |
| 3 | 1 | 3 | --- | 2 | 1 | 2 | E | 15757.1509 ^e | 0.0021 |
| 3 | 1 | 2 | --- | 2 | 1 | 1 | A | 16344.7522 ^e | -0.0041 |
| 3 | 1 | 2 | --- | 2 | 1 | 1 | E | 16344.7137 ^e | 0.0015 |
| 3 | 2 | 2 | --- | 2 | 2 | 1 | A | 16058.3228 ^e | -0.0032 |
| 3 | 2 | 2 | --- | 2 | 2 | 1 | E | 16058.4117 ^e | -0.0039 |
| 3 | 2 | 1 | --- | 2 | 2 | 0 | A | 16105.4747 ^e | -0.0033 |
| 3 | 2 | 1 | --- | 2 | 2 | 0 | E | 16105.2352 ^e | -0.0019 |

| | | | | | | | | | |
|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 4 | 0 | 4 | --- | 3 | 0 | 3 | A | 21295.2060 ^c | 0.0005 |
| 4 | 0 | 4 | --- | 3 | 0 | 3 | E | 21295.0609 ^c | 0.0011 |
| 4 | 1 | 4 | --- | 3 | 1 | 3 | A | 20996.7501 ^c | 0.0003 |
| 4 | 1 | 4 | --- | 3 | 1 | 3 | E | 20996.5859 ^c | 0.0026 |
| 4 | 1 | 3 | --- | 3 | 1 | 2 | A | 21777.9587 ^c | -0.0024 |
| 4 | 1 | 3 | --- | 3 | 1 | 2 | E | 21777.8990 ^c | 0.0007 |
| 4 | 2 | 3 | --- | 3 | 2 | 2 | A | 21401.7059 ^c | -0.0005 |
| 4 | 2 | 3 | --- | 3 | 2 | 2 | E | 21401.6244 ^c | 0.0009 |
| 4 | 2 | 2 | --- | 3 | 2 | 1 | A | 21517.7598 ^c | -0.0036 |
| 4 | 2 | 2 | --- | 3 | 2 | 1 | E | 21517.6554 ^c | 0.0016 |
| 4 | 3 | 2 | --- | 3 | 3 | 1 | A | 21433.2262 ^c | -0.0009 |
| 4 | 3 | 2 | --- | 3 | 3 | 1 | E | 21434.0235 ^c | 0.0021 |
| 4 | 3 | 1 | --- | 3 | 3 | 0 | A | 21435.9198 ^c | -0.0045 |
| 4 | 3 | 1 | --- | 3 | 3 | 0 | E | 21434.9231 ^c | -0.0012 |

c-type transition

| | | | | | | | | | |
|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 1 | 1 | 0 | --- | 0 | 0 | 0 | A | 7879.8114 ^c | -0.0025 |
| 1 | 1 | 0 | --- | 0 | 0 | 0 | E | 7879.7974 ^c | -0.0026 |
| 2 | 0 | 2 | --- | 1 | 1 | 0 | A | 8166.8936 ^c | 0.0068 |
| 2 | 0 | 2 | --- | 1 | 1 | 0 | E | 8166.8159 ^c | 0.0024 |
| 2 | 1 | 1 | --- | 1 | 0 | 1 | A | 13428.6000 ^c | -0.0049 |
| 2 | 1 | 1 | --- | 1 | 0 | 1 | E | 13428.5837 ^c | -0.0053 |
| 2 | 2 | 0 | --- | 1 | 1 | 0 | A | 17906.4360 | 0.0126 |
| 2 | 2 | 0 | --- | 1 | 1 | 0 | E | 17906.5562 ^c | -0.0035 |
| 2 | 2 | 1 | --- | 1 | 1 | 1 | A | 18090.5550 | 0.0111 |
| 2 | 2 | 1 | --- | 1 | 1 | 1 | E | 18090.2740 ^c | -0.0057 |
| 2 | 2 | 1 | --- | 2 | 1 | 1 | A | 6992.9015 | -0.0130 |
| 2 | 2 | 1 | --- | 2 | 1 | 1 | E | 6992.6435 ^c | -0.0030 |
| 2 | 2 | 0 | --- | 2 | 1 | 2 | A | 7592.7189 | 0.0067 |
| 2 | 2 | 0 | --- | 2 | 1 | 2 | E | 7592.9573 ^c | -0.0041 |
| 3 | 0 | 3 | --- | 2 | 1 | 1 | A | 13276.5859 | -0.0121 |
| 3 | 0 | 3 | --- | 2 | 1 | 1 | E | 13276.4614 ^c | 0.0045 |
| 3 | 1 | 2 | --- | 2 | 0 | 2 | A | 19079.5120 ^e | -0.0071 |
| 3 | 1 | 2 | --- | 2 | 0 | 2 | E | 19079.5120 ^c | -0.0064 |
| 3 | 1 | 3 | --- | 2 | 2 | 1 | A | 8176.4315 ^c | 0.0126 |

| | | | | | | | | | |
|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 3 | 1 | 3 | --- | 2 | 2 | 1 | E | 8176.4789 | -0.0020 |
| 3 | 1 | 2 | --- | 2 | 2 | 0 | A | 9339.9766 ^c | -0.0060 |
| 3 | 1 | 2 | --- | 2 | 2 | 0 | E | 9339.7839 | 0.0117 |
| 3 | 2 | 1 | --- | 2 | 1 | 1 | A | 23110.2634 | 0.0116 |
| 3 | 2 | 1 | --- | 2 | 1 | 1 | E | 23110.1753 ^c | -0.0018 |
| 3 | 2 | 2 | --- | 2 | 1 | 2 | A | 23639.1905 | 0.0116 |
| 3 | 2 | 2 | --- | 2 | 1 | 2 | E | 23639.0769 ^c | -0.0066 |
| 3 | 2 | 2 | --- | 3 | 1 | 2 | A | 6706.4836 ^c | -0.0006 |
| 3 | 2 | 2 | --- | 3 | 1 | 2 | E | 6706.3478 ^c | -0.0021 |
| 3 | 2 | 1 | --- | 3 | 1 | 3 | A | 7940.9304 | 0.0121 |
| 3 | 2 | 1 | --- | 3 | 1 | 3 | E | 7941.0421 ^c | -0.0077 |
| 3 | 3 | 1 | --- | 3 | 2 | 1 | A | 12093.0629 | 0.0052 |
| 3 | 3 | 1 | --- | 3 | 2 | 1 | E | 12090.7846 | 0.0066 |
| 3 | 3 | 0 | --- | 3 | 2 | 2 | A | 12152.5286 | 0.0090 |
| 3 | 3 | 0 | --- | 3 | 2 | 2 | E | 12154.7384 | -0.0131 |
| 3 | 3 | 1 | --- | 3 | 2 | 2 | E | 12149.8991 | 0.0061 |
| 3 | 3 | 0 | --- | 3 | 2 | 1 | E | 12095.6236 | -0.0129 |
| 4 | 1 | 4 | --- | 3 | 2 | 2 | A | 13114.8354 | -0.0073 |
| 4 | 1 | 4 | --- | 3 | 2 | 2 | E | 13114.6581 ^c | 0.0095 |
| 4 | 1 | 3 | --- | 3 | 2 | 1 | A | 15012.4633 ^c | -0.0023 |
| 4 | 1 | 3 | --- | 3 | 2 | 1 | E | 15012.4368 ^c | 0.0034 |
| 4 | 0 | 4 | --- | 3 | 1 | 2 | A | 18227.0405 | -0.0066 |
| 4 | 0 | 4 | --- | 3 | 1 | 2 | E | 18226.8120 ^c | 0.0074 |
| 4 | 2 | 3 | --- | 4 | 1 | 3 | A | 6330.2298 ^c | 0.0003 |
| 4 | 2 | 3 | --- | 4 | 1 | 3 | E | 6330.0765 ^c | 0.0014 |
| 4 | 2 | 2 | --- | 4 | 1 | 4 | A | 8461.9388 | 0.0069 |
| 4 | 2 | 2 | --- | 4 | 1 | 4 | E | 8462.1099 ^c | -0.0104 |
| 4 | 3 | 2 | --- | 4 | 2 | 2 | A | 12008.5226 ^c | 0.0012 |
| 4 | 3 | 2 | --- | 4 | 2 | 2 | E | 12007.1490 | 0.0034 |
| 4 | 3 | 1 | --- | 4 | 2 | 3 | A | 12186.7359 ^c | -0.0016 |
| 4 | 3 | 1 | --- | 4 | 2 | 3 | E | 12188.0504 | 0.0019 |
| 4 | 3 | 2 | --- | 4 | 2 | 3 | E | 12182.2934 | 0.0025 |
| 4 | 3 | 1 | --- | 4 | 2 | 2 | E | 12012.8979 | -0.0091 |
| 4 | 4 | 1 | --- | 4 | 3 | 1 | A | 16979.3372 ^c | -0.0089 |
| 4 | 4 | 0 | --- | 4 | 3 | 2 | A | 16982.5210 | 0.0129 |

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|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 4 | 4 | 0 | --- | 4 | 3 | 2 | E | 16986.9970 | -0.0021 |
| 4 | 4 | 1 | --- | 4 | 3 | 2 | E | 16980.5560 ^c | 0.0015 |
| 5 | 1 | 5 | --- | 4 | 2 | 3 | A | 17939.5348 | -0.0040 |
| 5 | 1 | 5 | --- | 4 | 2 | 3 | E | 17939.2261 ^c | 0.0091 |
| 5 | 1 | 4 | --- | 4 | 2 | 2 | A | 20691.5808 ^c | -0.0075 |
| 5 | 1 | 4 | --- | 4 | 2 | 2 | E | 20691.5808 ^c | 0.0010 |
| 5 | 0 | 5 | --- | 4 | 1 | 3 | A | 22987.9221 | -0.0067 |
| 5 | 0 | 5 | --- | 4 | 1 | 3 | E | 22987.5538 ^c | 0.0093 |
| 5 | 2 | 4 | --- | 5 | 1 | 4 | A | 5870.4146 ^c | 0.0054 |
| 5 | 2 | 4 | --- | 5 | 1 | 4 | E | 5870.2068 ^c | 0.0017 |
| 5 | 2 | 3 | --- | 5 | 1 | 5 | A | 9197.6476 | 0.0312 |
| 5 | 2 | 3 | --- | 5 | 1 | 5 | E | 9197.9101 ^c | -0.0125 |
| 5 | 3 | 3 | --- | 5 | 2 | 3 | A | 11845.9551 | 0.0222 |
| 5 | 3 | 3 | --- | 5 | 2 | 3 | E | 11845.3783 ^c | -0.0061 |
| 5 | 3 | 2 | --- | 5 | 2 | 4 | A | 12258.5619 ^c | -0.0015 |
| 5 | 3 | 2 | --- | 5 | 2 | 4 | E | 12259.0282 ^c | -0.0007 |
| 5 | 4 | 2 | --- | 5 | 3 | 2 | A | 16959.7875 ^c | -0.0006 |
| 5 | 4 | 2 | --- | 5 | 3 | 2 | E | 16956.1352 ^c | -0.0210 |
| 5 | 4 | 1 | --- | 5 | 3 | 3 | A | 16972.4606 ^c | 0.0033 |
| 5 | 4 | 1 | --- | 5 | 3 | 3 | E | 16976.0134 | -0.0059 |
| 5 | 4 | 2 | --- | 5 | 3 | 3 | E | 16969.5990 | 0.0076 |
| 5 | 4 | 1 | --- | 5 | 3 | 2 | E | 16962.5784 | -0.0057 |
| 5 | 5 | 1 | --- | 5 | 4 | 1 | A | 21836.4460 | 0.0044 |
| 5 | 5 | 0 | --- | 5 | 4 | 2 | A | 21836.5776 | 0.0075 |
| 5 | 5 | 1 | --- | 5 | 4 | 2 | E | 21835.6525 ^c | -0.0050 |
| 5 | 5 | 0 | --- | 5 | 4 | 1 | E | 21837.2765 ^c | 0.0001 |
| 6 | 2 | 4 | --- | 5 | 3 | 2 | A | 20577.9978 ^c | -0.0038 |
| 6 | 1 | 6 | --- | 5 | 2 | 4 | A | 22647.7053 | -0.0059 |
| 6 | 1 | 6 | --- | 5 | 2 | 4 | E | 22647.2801 ^c | 0.0087 |
| 6 | 2 | 4 | --- | 6 | 1 | 6 | A | 10188.8883 | 0.0344 |
| 6 | 2 | 4 | --- | 6 | 1 | 6 | E | 10189.3154 ^c | -0.0108 |
| 6 | 2 | 5 | --- | 6 | 1 | 5 | A | 5336.6368 ^c | 0.0028 |
| 6 | 2 | 5 | --- | 6 | 1 | 5 | E | 5336.3711 ^c | 0.0012 |
| 6 | 3 | 4 | --- | 6 | 2 | 4 | A | 11578.3326 ^c | 0.0036 |
| 6 | 3 | 4 | --- | 6 | 2 | 4 | E | 11578.0061 ^c | -0.0035 |

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|---|---|---|-----|---|---|---|---|-------------------------|---------|
| 6 | 3 | 3 | --- | 6 | 2 | 5 | A | 12389.7733 ^c | -0.0013 |
| 6 | 3 | 3 | --- | 6 | 2 | 5 | E | 12389.9779 ^c | -0.0048 |
| 6 | 4 | 3 | --- | 6 | 3 | 3 | A | 16921.5053 ^c | 0.0012 |
| 6 | 4 | 3 | --- | 6 | 3 | 3 | E | 16918.4008 | -0.0031 |
| 6 | 4 | 2 | --- | 6 | 3 | 4 | A | 16959.5051 ^c | 0.0014 |
| 6 | 4 | 2 | --- | 6 | 3 | 4 | E | 16962.5153 | -0.0046 |
| 6 | 4 | 3 | --- | 6 | 3 | 4 | E | 16956.0682 | -0.0162 |
| 6 | 4 | 2 | --- | 6 | 3 | 3 | E | 16924.8588 | 0.0194 |
| 6 | 5 | 2 | --- | 6 | 4 | 2 | A | 21825.0150 | -0.0105 |
| 6 | 5 | 1 | --- | 6 | 4 | 3 | A | 21825.6707 ^c | 0.0018 |
| 6 | 5 | 2 | --- | 6 | 4 | 3 | E | 21824.5078 ^c | -0.0045 |
| 6 | 5 | 1 | --- | 6 | 4 | 2 | E | 21826.1003 ^c | 0.0016 |
| 7 | 2 | 6 | --- | 7 | 1 | 6 | A | 4742.9576 ^c | 0.0020 |
| 7 | 2 | 6 | --- | 7 | 1 | 6 | E | 4742.6294 ^c | -0.0009 |
| 7 | 2 | 5 | --- | 7 | 1 | 7 | E | 11468.0946 ^c | -0.0106 |
| 7 | 3 | 5 | --- | 7 | 2 | 5 | A | 11186.7583 ^c | 0.0012 |
| 7 | 3 | 5 | --- | 7 | 2 | 5 | E | 11186.4384 ^c | -0.0029 |
| 7 | 3 | 4 | --- | 7 | 2 | 6 | A | 12608.6495 ^c | -0.0006 |
| 7 | 3 | 4 | --- | 7 | 2 | 6 | E | 12608.8249 ^c | -0.0047 |
| 7 | 4 | 4 | --- | 7 | 3 | 4 | A | 16852.1996 ^c | 0.0022 |
| 7 | 4 | 4 | --- | 7 | 3 | 4 | E | 16849.8342 | -0.0025 |
| 7 | 4 | 3 | --- | 7 | 3 | 5 | A | 16946.8791 ^c | 0.0011 |
| 7 | 4 | 3 | --- | 7 | 3 | 5 | E | 16949.1388 | 0.0068 |
| 7 | 4 | 4 | --- | 7 | 3 | 5 | E | 16942.3399 | -0.0031 |
| 7 | 4 | 3 | --- | 7 | 3 | 4 | E | 16856.6204 | -0.0053 |
| 7 | 5 | 3 | --- | 7 | 4 | 3 | A | 21806.5866 ^c | 0.0018 |
| 7 | 5 | 2 | --- | 7 | 4 | 4 | A | 21808.9538 ^c | 0.0081 |
| 7 | 5 | 3 | --- | 7 | 4 | 4 | E | 21807.1096 ^c | -0.0081 |
| 7 | 5 | 2 | --- | 7 | 4 | 3 | E | 21808.3171 ^c | -0.0035 |
| 8 | 4 | 5 | --- | 8 | 3 | 5 | A | 16734.5266 ^c | 0.0014 |
| 8 | 4 | 4 | --- | 8 | 3 | 6 | A | 16941.1435 ^c | 0.0010 |
| 8 | 4 | 4 | --- | 8 | 3 | 6 | E | 16942.3613 | -0.0068 |
| 8 | 5 | 3 | --- | 8 | 4 | 5 | A | 21785.1191 ^c | 0.0059 |
| 8 | 5 | 4 | --- | 8 | 4 | 5 | E | 21782.2564 | 0.0049 |
| 8 | 5 | 3 | --- | 8 | 4 | 4 | E | 21780.7883 | -0.0012 |

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| 9 | 4 | 6 | --- | 9 | 3 | 6 | A | 16545.9584 ^e | -0.0006 |
| 9 | 4 | 6 | --- | 9 | 3 | 6 | E | 16545.2239 ^e | -0.0087 |
| 9 | 4 | 5 | --- | 9 | 3 | 7 | A | 16953.1520 ^e | 0.0005 |
| 9 | 4 | 5 | --- | 9 | 3 | 7 | E | 16953.6858 ^e | -0.0026 |
| 9 | 5 | 5 | --- | 9 | 4 | 5 | A | 21734.9931 ^e | 0.0037 |
| 9 | 5 | 4 | --- | 9 | 4 | 6 | A | 21753.3588 ^e | 0.0044 |
| 10 | 4 | 7 | --- | 10 | 3 | 7 | A | 16260.2334 ^e | -0.0042 |
| 10 | 4 | 7 | --- | 10 | 3 | 7 | E | 16259.7267 | 0.0025 |
| 10 | 4 | 6 | --- | 10 | 3 | 8 | A | 16998.9664 ^e | 0.0021 |
| 10 | 4 | 6 | --- | 10 | 3 | 8 | E | 16999.2225 ^e | -0.0031 |
| 10 | 5 | 6 | --- | 10 | 4 | 6 | A | 21671.1428 ^e | 0.0015 |
| 10 | 5 | 5 | --- | 10 | 4 | 7 | A | 21713.7933 ^e | 0.0023 |

^a Angle between the internal-rotation axis and the *a*, *b*, *c*-inertial axes.

^b Fixed.

^c Standard deviation of the fit.

^d Values in parentheses denote one standard deviation.

^e Overlapped with the ground-state transition.