

# Supplementary Material

## Conformational sampling and large amplitude motions of methyl valerate

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**Table S-1a.** Geometry parameters in the principal axes of inertia of the seven lowest energy conformers of methyl valerate calculated at the MP2/6-311++G(d,p) level of theory. The atoms are numbered according to Figure 2.

| <b>Conformer I</b> |                  |                  |                  | <b>Conformer II</b> |                  |                  |  |
|--------------------|------------------|------------------|------------------|---------------------|------------------|------------------|--|
|                    | $a / \text{\AA}$ | $b / \text{\AA}$ | $c / \text{\AA}$ | $a / \text{\AA}$    | $b / \text{\AA}$ | $c / \text{\AA}$ |  |
| C1                 | -0.936038        | 0.214300         | 0.261254         | -0.753729           | 0.233034         | 0.497059         |  |
| O2                 | -0.894706        | -0.569192        | 1.186556         | -0.925722           | 1.433067         | 0.438965         |  |
| O3                 | -1.947515        | 0.253812         | -0.635965        | -1.561061           | -0.663642        | -0.118187        |  |
| C4                 | -2.994251        | -0.698864        | -0.387373        | -2.645749           | -0.076468        | -0.854164        |  |
| H5                 | -3.723437        | -0.539216        | -1.179398        | -3.199176           | -0.915249        | -1.272418        |  |
| H6                 | -2.600418        | -1.716030        | -0.425114        | -3.281559           | 0.513029         | -0.191196        |  |
| H7                 | -3.443765        | -0.524979        | 0.591888         | -2.263361           | 0.567636         | -1.648425        |  |
| C8                 | 0.098266         | 1.278601         | -0.025354        | 0.374469            | -0.467208        | 1.212586         |  |
| H9                 | 0.032321         | 1.570086         | -1.077619        | 0.920283            | 0.288832         | 1.780267         |  |
| H10                | -0.182236        | 2.154289         | 0.573420         | -0.050880           | -1.190224        | 1.916338         |  |
| C11                | 1.507216         | 0.810443         | 0.339290         | 1.296856            | -1.196111        | 0.220632         |  |
| H12                | 2.196042         | 1.659764         | 0.252880         | 2.141991            | -1.614386        | 0.781533         |  |
| H13                | 1.515920         | 0.487056         | 1.386068         | 0.749042            | -2.036424        | -0.218032        |  |
| C14                | 1.998018         | -0.331147        | -0.551851        | 1.827091            | -0.291353        | -0.896088        |  |
| H15                | 1.307284         | -1.178363        | -0.465380        | 2.454183            | -0.896344        | -1.561557        |  |
| H16                | 1.974077         | -0.003546        | -1.599373        | 0.987789            | 0.065574         | -1.507243        |  |
| C17                | 3.410542         | -0.786434        | -0.184680        | 2.630054            | 0.905524         | -0.382280        |  |
| H18                | 3.443279         | -1.140563        | 0.850645         | 3.437978            | 0.573655         | 0.279601         |  |
| H19                | 3.749086         | -1.600887        | -0.831866        | 3.081002            | 1.456702         | -1.212714        |  |
| H20                | 4.122226         | 0.040281         | -0.281011        | 1.996124            | 1.603693         | 0.171071         |  |

  

| <b>Conformer III</b> |                  |                  |                  | <b>Conformer IV</b> |                  |                  |  |
|----------------------|------------------|------------------|------------------|---------------------|------------------|------------------|--|
|                      | $a / \text{\AA}$ | $b / \text{\AA}$ | $c / \text{\AA}$ | $a / \text{\AA}$    | $b / \text{\AA}$ | $c / \text{\AA}$ |  |
| C1                   | -1.022180        | -0.536110        | 0.071805         | -0.828273           | -0.524018        | 0.175194         |  |
| O2                   | -1.576222        | -0.837551        | 1.107976         | -1.333811           | -1.220528        | -0.680215        |  |
| O3                   | -1.328735        | 0.576849         | -0.637516        | -1.295149           | 0.702290         | 0.508818         |  |
| C4                   | -2.373268        | 1.376575         | -0.061287        | -2.450176           | 1.116482         | -0.239505        |  |
| H5                   | -2.501556        | 2.217928         | -0.739871        | -2.700184           | 2.105708         | 0.139412         |  |
| H6                   | -3.296584        | 0.799681         | 0.016867         | -2.218480           | 1.158319         | -1.305440        |  |
| H7                   | -2.083743        | 1.723149         | 0.932624         | -3.276659           | 0.421721         | -0.080039        |  |
| C8                   | 0.084205         | -1.310256        | -0.603186        | 0.403827            | -0.888261        | 0.966284         |  |
| H9                   | 0.292457         | -2.184142        | 0.019619         | 0.588397            | -0.135086        | 1.734478         |  |
| H10                  | -0.285585        | -1.656284        | -1.574926        | 0.205051            | -1.845187        | 1.459674         |  |
| C11                  | 1.348244         | -0.461376        | -0.793860        | 1.607466            | -1.039495        | 0.022450         |  |
| H12                  | 2.116463         | -1.081961        | -1.271871        | 2.485109            | -1.315189        | 0.620254         |  |
| H13                  | 1.128917         | 0.366748         | -1.476652        | 1.406106            | -1.868567        | -0.664505        |  |
| C14                  | 1.893086         | 0.091104         | 0.523383         | 1.916013            | 0.227129         | -0.782186        |  |
| H15                  | 1.132855         | 0.727079         | 0.994290         | 2.763064            | 0.015898         | -1.445470        |  |
| H16                  | 2.075386         | -0.740846        | 1.215541         | 1.066578            | 0.458785         | -1.437841        |  |
| C17                  | 3.177875         | 0.895725         | 0.325963         | 2.241769            | 1.441412         | 0.090044         |  |
| H18                  | 3.004036         | 1.741994         | -0.346704        | 3.055511            | 1.210026         | 0.786593         |  |
| H19                  | 3.552612         | 1.289513         | 1.275274         | 2.557726            | 2.289444         | -0.524946        |  |
| H20                  | 3.962556         | 0.271899         | -0.114594        | 1.373105            | 1.760985         | 0.672305         |  |

**Table S-1a. continued**

| <b>Conformer V</b> |                |                |                | <b>Conformer VI</b> |                |                |  |
|--------------------|----------------|----------------|----------------|---------------------|----------------|----------------|--|
|                    | $a / \text{Å}$ | $b / \text{Å}$ | $c / \text{Å}$ | $a / \text{Å}$      | $b / \text{Å}$ | $c / \text{Å}$ |  |
| C1                 | 1.115132       | 0.110765       | -0.000022      | -0.706491           | -0.471642      | 0.118745       |  |
| O2                 | 1.214904       | 1.319088       | -0.000068      | -0.844397           | -0.405682      | 1.321831       |  |
| O3                 | 2.180751       | -0.725048      | 0.000041       | -1.593741           | 0.048310       | -0.761470      |  |
| C4                 | 3.454065       | -0.060831      | 0.000061       | -2.723489           | 0.690472       | -0.148448      |  |
| H5                 | 4.195390       | -0.857767      | 0.000169       | -3.335043           | 1.048838       | -0.974461      |  |
| H6                 | 3.559580       | 0.562971       | -0.889373      | -3.280884           | -0.019983      | 0.464614       |  |
| H7                 | 3.559475       | 0.563121       | 0.889402       | -2.394220           | 1.522279       | 0.477291       |  |
| C8                 | -0.177462      | -0.671608      | -0.000072      | 0.435016            | -1.163909      | -0.589475      |  |
| H9                 | -0.169345      | -1.330517      | -0.876614      | 0.189997            | -2.233207      | -0.573387      |  |
| H10                | -0.169310      | -1.330703      | 0.876328       | 0.459093            | -0.850087      | -1.637297      |  |
| C11                | -1.412418      | 0.222750       | 0.000036       | 1.786142            | -0.930461      | 0.096128       |  |
| H12                | -1.383490      | 0.879305       | 0.877191       | 1.650500            | -1.023898      | 1.179549       |  |
| H13                | -1.383483      | 0.879526       | -0.876952      | 2.475034            | -1.724591      | -0.213014      |  |
| C14                | -2.711481      | -0.582757      | -0.000066      | 2.414667            | 0.425760       | -0.241707      |  |
| H15                | -2.730231      | -1.238276      | -0.880124      | 3.385084            | 0.492566       | 0.264533       |  |
| H16                | -2.730211      | -1.238536      | 0.879799       | 2.622323            | 0.462180       | -1.319263      |  |
| C17                | -3.950313      | 0.313453       | 0.000084       | 1.557546            | 1.631729       | 0.150893       |  |
| H18                | -3.960904      | 0.958238       | -0.884598      | 1.291900            | 1.594148       | 1.211882       |  |
| H19                | -4.871477      | -0.276713      | 0.000009       | 2.097736            | 2.564991       | -0.035482      |  |
| H20                | -3.960882      | 0.957981       | 0.884953       | 0.630267            | 1.672086       | -0.429132      |  |

| <b>Conformer VII</b> |                |                |                |
|----------------------|----------------|----------------|----------------|
|                      | $a / \text{Å}$ | $b / \text{Å}$ | $c / \text{Å}$ |
| C1                   | -1.168247      | 0.443690       | 0.128402       |
| O2                   | -1.682989      | 1.298886       | -0.561574      |
| O3                   | -1.738770      | -0.760554      | 0.372290       |
| C4                   | -3.003626      | -0.958291      | -0.278866      |
| H5                   | -3.329817      | -1.953013      | 0.019087       |
| H6                   | -3.721864      | -0.203527      | 0.046064       |
| H7                   | -2.887849      | -0.898909      | -1.362721      |
| C8                   | 0.192595       | 0.535264       | 0.767506       |
| H9                   | 0.396352       | 1.590155       | 0.970717       |
| H10                  | 0.196988       | -0.023348      | 1.707851       |
| C11                  | 1.260638       | -0.030722      | -0.181327      |
| H12                  | 1.026376       | -1.079870      | -0.400719      |
| H13                  | 1.220540       | 0.517790       | -1.130936      |
| C14                  | 2.669037       | 0.066051       | 0.404477       |
| H15                  | 2.891291       | 1.116250       | 0.631254       |
| H16                  | 2.698968       | -0.477050      | 1.357408       |
| C17                  | 3.729826       | -0.494163      | -0.543561      |
| H18                  | 3.727817       | 0.051925       | -1.492398      |
| H19                  | 4.731923       | -0.417677      | -0.111554      |
| H20                  | 3.535288       | -1.549215      | -0.761886      |

**Table S-1b.** Geometry parameters in the principal axes of inertia of the seven lowest energy conformers of methyl valerate calculated at the MP2/cc-pVDZ level of theory. The atoms are numbered according to Figure 1.

| <b>Conformer I</b> |                |                |                | <b>Conformer II</b> |                |                |  |
|--------------------|----------------|----------------|----------------|---------------------|----------------|----------------|--|
|                    | $a / \text{Å}$ | $b / \text{Å}$ | $c / \text{Å}$ | $a / \text{Å}$      | $b / \text{Å}$ | $c / \text{Å}$ |  |
| C1                 | -0.937631      | 0.091490       | 0.201162       | -0.736139           | 0.156101       | 0.541880       |  |
| O2                 | -0.773302      | -0.991453      | 0.730932       | -0.898220           | 1.355468       | 0.667367       |  |
| O3                 | -2.096400      | 0.464677       | -0.397775      | -1.555564           | -0.637433      | -0.197496      |  |
| C4                 | -3.126810      | -0.535000      | -0.335420      | -2.631028           | 0.074112       | -0.830995      |  |
| H5                 | -3.990653      | -0.100862      | -0.854452      | -3.195097           | -0.681727      | -1.392062      |  |
| H6                 | -2.802769      | -1.461429      | -0.833827      | -3.275077           | 0.557974       | -0.080761      |  |
| H7                 | -3.382296      | -0.769037      | 0.709496       | -2.240653           | 0.847603       | -1.510334      |  |
| C8                 | 0.081371       | 1.211786       | 0.137507       | 0.392910            | -0.657498      | 1.133167       |  |
| H9                 | 0.036988       | 1.666856       | -0.866923      | 0.951009            | 0.001317       | 1.814785       |  |
| H10                | -0.261439      | 1.991117       | 0.842500       | -0.039090           | -1.482616      | 1.724587       |  |
| C11                | 1.493186       | 0.738654       | 0.484188       | 1.303241            | -1.235693      | 0.033742       |  |
| H12                | 2.145342       | 1.621485       | 0.615304       | 2.162698            | -1.733301      | 0.520040       |  |
| H13                | 1.463557       | 0.208473       | 1.452632       | 0.745764            | -2.014737      | -0.514365      |  |
| C14                | 2.096229       | -0.183299      | -0.579608      | 1.814056            | -0.180905      | -0.957726      |  |
| H15                | 1.445269       | -1.066520      | -0.701958      | 2.477109            | -0.679887      | -1.687560      |  |
| H16                | 2.109156       | 0.345534       | -1.551920      | 0.960350            | 0.214031       | -1.540761      |  |
| C17                | 3.512987       | -0.636404      | -0.220817      | 2.556753            | 0.981293       | -0.291575      |  |
| H18                | 3.516035       | -1.188810      | 0.734451       | 3.375305            | 0.609990       | 0.350392       |  |
| H19                | 3.934402       | -1.298286      | -0.995275      | 2.999262            | 1.651066       | -1.047382      |  |
| H20                | 4.189314       | 0.229106       | -0.110770      | 1.875823            | 1.585260       | 0.329687       |  |

  

| <b>Conformer III</b> |                |                |                | <b>Conformer IV</b> |                |                |  |
|----------------------|----------------|----------------|----------------|---------------------|----------------|----------------|--|
|                      | $a / \text{Å}$ | $b / \text{Å}$ | $c / \text{Å}$ | $a / \text{Å}$      | $b / \text{Å}$ | $c / \text{Å}$ |  |
| C1                   | -1.048437      | -0.535905      | 0.060227       | -0.796426           | -0.519608      | 0.155457       |  |
| O2                   | -1.697534      | -0.872492      | 1.031223       | -1.204111           | -1.197799      | -0.768435      |  |
| O3                   | -1.255078      | 0.629120       | -0.611316      | -1.375269           | 0.647115       | 0.543077       |  |
| C4                   | -2.311540      | 1.431875       | -0.060882      | -2.526281           | 1.006087       | -0.240408      |  |
| H5                   | -2.355293      | 2.332063       | -0.687098      | -2.882141           | 1.956443       | 0.176968       |  |
| H6                   | -3.270570      | 0.892290       | -0.093685      | -2.253818           | 1.126524       | -1.300167      |  |
| H7                   | -2.094671      | 1.699171       | 0.984843       | -3.306372           | 0.233374       | -0.163403      |  |
| C8                   | 0.076658       | -1.323830      | -0.577634      | 0.419551            | -0.839056      | 0.998055       |  |
| H9                   | 0.264614       | -2.195748      | 0.068703       | 0.562428            | -0.055110      | 1.756168       |  |
| H10                  | -0.285300      | -1.694378      | -1.553221      | 0.214960            | -1.787235      | 1.524758       |  |
| C11                  | 1.350537       | -0.490486      | -0.774823      | 1.660583            | -1.008467      | 0.106024       |  |
| H12                  | 2.121104       | -1.126318      | -1.248678      | 2.529241            | -1.232838      | 0.752059       |  |
| H13                  | 1.137426       | 0.335268       | -1.476137      | 1.502529            | -1.885407      | -0.545605      |  |
| C14                  | 1.896871       | 0.080243       | 0.536550       | 1.966227            | 0.219962       | -0.762658      |  |
| H15                  | 1.132215       | 0.735040       | 0.994804       | 2.886553            | 0.018760       | -1.340256      |  |
| H16                  | 2.069670       | -0.746415      | 1.251371       | 1.159394            | 0.345249       | -1.509094      |  |
| C17                  | 3.190680       | 0.871866       | 0.334592       | 2.131575            | 1.515861       | 0.037277       |  |
| H18                  | 3.029704       | 1.715291       | -0.358748      | 2.888236            | 1.396405       | 0.833020       |  |
| H19                  | 3.566676       | 1.282416       | 1.286101       | 2.456797            | 2.343695       | -0.614506      |  |
| H20                  | 3.981221       | 0.231798       | -0.093762      | 1.182109            | 1.817464       | 0.509055       |  |

**Table S-1b. continued**

| Conformer V |                  |                  | Conformer VI     |                  |                  |                  |
|-------------|------------------|------------------|------------------|------------------|------------------|------------------|
|             | $a / \text{\AA}$ | $b / \text{\AA}$ | $c / \text{\AA}$ | $a / \text{\AA}$ | $b / \text{\AA}$ | $c / \text{\AA}$ |
| C1          | 1.117217         | 0.107284         | -0.000030        | -0.702670        | -0.488558        | 0.105914         |
| O2          | 1.210499         | 1.319792         | -0.000049        | -0.852414        | -0.466107        | 1.312831         |
| O3          | 2.186647         | -0.729221        | 0.000030         | -1.574855        | 0.075753         | -0.768571        |
| C4          | 3.452047         | -0.048968        | 0.000054         | -2.703288        | 0.699151         | -0.132248        |
| H5          | 4.212384         | -0.840197        | 0.000116         | -3.315346        | 1.103604         | -0.948319        |
| H6          | 3.555727         | 0.585054         | -0.893889        | -3.276413        | -0.035217        | 0.454156         |
| H7          | 3.555656         | 0.585125         | 0.893958         | -2.372519        | 1.506072         | 0.539649         |
| C8          | -0.175192        | -0.681657        | -0.000064        | 0.446660         | -1.160444        | -0.617891        |
| H9          | -0.162683        | -1.348913        | -0.880819        | 0.212996         | -2.240823        | -0.617777        |
| H10         | -0.162649        | -1.349064        | 0.880573         | 0.466703         | -0.830921        | -1.669485        |
| C11         | -1.410464        | 0.215101         | 0.000027         | 1.791948         | -0.923553        | 0.082557         |
| H12         | -1.375476        | 0.880038         | 0.881771         | 1.637546         | -1.044134        | 1.169820         |
| H13         | -1.375487        | 0.880198         | -0.881596        | 2.502690         | -1.707634        | -0.232433        |
| C14         | -2.716723        | -0.581676        | -0.000035        | 2.405213         | 0.451657         | -0.215877        |
| H15         | -2.740600        | -1.245209        | -0.885118        | 3.370756         | 0.527514         | 0.316716         |
| H16         | -2.740585        | -1.245373        | 0.884924         | 2.641343         | 0.512097         | -1.295571        |
| C17         | -3.951750        | 0.321827         | 0.000059         | 1.516356         | 1.637265         | 0.174876         |
| H18         | -3.961028        | 0.973272         | -0.890575        | 1.224017         | 1.580488         | 1.236950         |
| H19         | -4.884358        | -0.266012        | 0.000012         | 2.043752         | 2.592060         | 0.012336         |
| H20         | -3.961014        | 0.973104         | 0.890816         | 0.592968         | 1.665939         | -0.427965        |

| Conformer VII |                  |                  |                  |
|---------------|------------------|------------------|------------------|
|               | $a / \text{\AA}$ | $b / \text{\AA}$ | $c / \text{\AA}$ |
| C1            | 1.207407         | 0.490026         | -0.067553        |
| O2            | 1.925503         | 1.266652         | 0.532136         |
| O3            | 1.562804         | -0.791440        | -0.353930        |
| C4            | 2.866973         | -1.150409        | 0.129091         |
| H5            | 3.013086         | -2.197380        | -0.165556        |
| H6            | 3.641004         | -0.511240        | -0.322802        |
| H7            | 2.921039         | -1.046537        | 1.223711         |
| C8            | -0.189058        | 0.772483         | -0.573527        |
| H9            | -0.378734        | 1.848539         | -0.436570        |
| H10           | -0.225433        | 0.542143         | -1.652704        |
| C11           | -1.244714        | -0.066601        | 0.162533         |
| H12           | -1.014603        | -1.137577        | 0.020706         |
| H13           | -1.175506        | 0.134548         | 1.248704         |
| C14           | -2.667678        | 0.226805         | -0.318465        |
| H15           | -2.884147        | 1.302775         | -0.181288        |
| H16           | -2.729188        | 0.032478         | -1.405796        |
| C17           | -3.716493        | -0.610170        | 0.417072         |
| H18           | -3.689639        | -0.408850        | 1.501753         |
| H19           | -4.734900        | -0.389795        | 0.057202         |
| H20           | -3.530977        | -1.688158        | 0.271196         |

**Table S-2.** The rotational constants  $A$ ,  $B$ ,  $C$  (in MHz), dipole moment components  $\mu_a$ ,  $\mu_b$ ,  $\mu_c$  (in Debye), the dihedral angles  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  (in degree), relative energies  $E_{rel.}$  (in  $\text{kJ}\cdot\text{mol}^{-1}$ ), and relative energies including zero-point energy corrections  $ZPE$ . (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) of the 11 *anti* conformers of methyl valerate calculated at the MP2/6-311++G(d,p) level of theory. All energies are relative to the lowest energy conformer I with its absolute energy of  $E = -385.3337699$  Hartree. The corresponding absolute energy including ZPE corrections is  $E = -385.3337699$  Hartree.

| Conf.                      | $A$           | $B$          | $C$          | $ \mu_a $ | $ \mu_b $ | $ \mu_c $ | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $E_{rel.}$ | $ZPE$ |
|----------------------------|---------------|--------------|--------------|-----------|-----------|-----------|------------|------------|------------|------------|-------|
| I                          | 4407.0        | 932.3        | 897.4        | 1.43      | 0.39      | 0.92      | 179.66     | 66.78      | -146.50    | 0.00       | 0.00  |
| II                         | 3372.9        | 1214.0       | 1147.9       | 0.43      | 0.03      | 2.02      | 59.17      | 53.77      | 64.33      | 0.77       | 1.84  |
| III                        | 3287.2        | 1099.1       | 1002.6       | 1.65      | 0.82      | 1.03      | 178.09     | 57.88      | 57.52      | 0.80       | 0.99  |
| IV                         | 3020.6        | 1344.4       | 1112.9       | 1.02      | 0.65      | 1.43      | 59.96      | 58.79      | -116.09    | 0.80       | 1.84  |
| V                          | 7537.1        | 739.8        | 688.0        | 0.00      | 0.16      | 1.80      | 180.00     | 180.00     | 180.00     | 2.93       | 1.63  |
| VI                         | 3372.8        | 1260.5       | 1132.6       | 1.72      | 0.00      | 0.16      | 59.68      | -80.07     | 141.16     | 2.98       | 3.70  |
| VII                        | 4930.2        | 808.4        | 765.4        | 0.84      | 0.80      | 1.76      | -179.83    | 178.70     | 86.95      | 3.01       | 2.82  |
| VIII                       | 5743.6        | 822.7        | 766.1        | 0.48      | 0.18      | 1.70      | 63.05      | 176.68     | -167.19    | 4.58       | 3.99  |
| IX                         | 4613.0        | 897.2        | 824.1        | 0.18      | 1.04      | 1.87      | 62.70      | 174.65     | 81.42      | 4.60       | 4.88  |
| X                          | 5357.0        | 860.3        | 799.8        | 0.44      | 0.56      | 1.98      | 62.34      | 176.78     | -89.86     | 4.79       | 5.05  |
| XI                         | 2920.7        | 1373.9       | 1241.3       | 2.00      | 0.75      | 0.45      | 67.50      | -70.58     | -49.67     | 5.03       | 5.59  |
| <b>Expt. C<sub>1</sub></b> | <b>5063.2</b> | <b>897.7</b> | <b>846.4</b> |           |           |           |            |            |            |            |       |
| <b>Expt. C<sub>s</sub></b> | <b>7545.3</b> | <b>739.5</b> | <b>688.5</b> |           |           |           |            |            |            |            |       |

**Table S-3.** The rotational constants  $A$ ,  $B$ ,  $C$  (in MHz) of conformer I of methyl valerate calculated at different levels of theory and their deviations to the experimental values (calc.–exp.)  $\Delta A$ ,  $\Delta B$ , and  $\Delta C$ , respectively (in MHz).

| Basis set                                     | $A$           | $\Delta A$ | $B$          | $\Delta B$  | $C$          | $\Delta C$  | $\theta$ |
|---|---------------|------------|--------------|-------------|--------------|-------------|----------|
| B3LYP-D3/6-311G(3df,3pd)                      | 5268.1        | 204.9      | 890.2        | -7.5        | 833.0        | -13.4       | 10.9     |
| <b>B3LYP-D3/6-311+G(3df,3pd)<sup>a</sup></b>  | <b>5071.5</b> | <b>8.3</b> | <b>893.2</b> | <b>-4.5</b> | <b>843.1</b> | <b>-3.3</b> | 16.7     |
| <b>B3LYP-D3/6-311++G(3df,3pd)<sup>a</sup></b> | <b>5068.0</b> | <b>4.8</b> | <b>893.4</b> | <b>-4.3</b> | <b>843.3</b> | <b>-3.1</b> | 16.7     |
| B3LYP-D3/6-311G(df,pd)                        | 5264.9        | 201.7      | 890.0        | -7.7        | 832.0        | -14.4       | 10.5     |
| B3LYP-D3/6-311+G(df,pd)                       | 5023.6        | -39.6      | 893.0        | -4.7        | 844.3        | -2.1        | 17.8     |
| B3LYP-D3/6-311++G(df,pd)                      | 5018.1        | -45.1      | 893.3        | -4.4        | 844.7        | -1.7        | 17.9     |
| B3LYP-D3/6-311G(d,p)                          | 5264.8        | 201.6      | 887.3        | -10.4       | 828.9        | -17.5       | 10.1     |
| B3LYP-D3/6-311+G(d,p)                         | 5020.8        | -42.4      | 890.3        | -7.4        | 841.3        | -5.1        | 17.5     |
| B3LYP-D3/6-311++G(d,p)                        | 5020.1        | -43.1      | 890.4        | -7.3        | 841.4        | -5.0        | 17.5     |
| B3LYP-D3/6-31G(d,p)                           | 5155.2        | 92.0       | 892.3        | -5.4        | 834.5        | -11.9       | 12.2     |
| B3LYP-D3/6-31+G(d,p)                          | 4959.5        | -103.7     | 889.8        | -7.9        | 841.9        | -4.5        | 18.7     |
| B3LYP-D3/6-31++G(d,p)                         | 4961.3        | -101.9     | 889.7        | -8.0        | 841.8        | -4.6        | 18.6     |
| B3LYP-D3/cc-pVDZ                              | 5274.8        | 211.6      | 887.5        | -10.2       | 826.7        | -19.7       | 16.4     |
| B3LYP-D3/cc-pVTZ                              | 5187.4        | 124.2      | 889.9        | -7.8        | 835.8        | -10.6       | 16.4     |
| B3LYP-D3/aug-cc-pVDZ                          | 5033.3        | -29.9      | 889.4        | -8.3        | 838.7        | -7.7        | 13.5     |
| B3LYP-D3/aug-cc-pVTZ                          | 5081.9        | 18.7       | 891.7        | -6.0        | 841.4        | -5.0        | 20.5     |
| B3LYP-D3BJ/6-311G(3df,3pd)                    | 5191.4        | 128.2      | 892.7        | -5.0        | 839.0        | -7.4        | 20.7     |
| B3LYP-D3BJ/6-311+G(3df,3pd)                   | 4946.9        | -116.3     | 897.5        | -0.2        | 852.6        | 6.2         | 13.4     |
| B3LYP-D3BJ/6-311++G(3df,3pd)                  | 4939.9        | -123.3     | 897.8        | 0.1         | 853.1        | 6.7         | 21.9     |
| B3LYP-D3BJ/6-311G(df,pd)                      | 5180.7        | 117.5      | 892.8        | -4.9        | 838.4        | -8.0        | 22.1     |
| B3LYP-D3BJ/6-311+G(df,pd)                     | 4886.6        | -176.6     | 897.8        | 0.1         | 854.7        | 8.3         | 12.9     |
| B3LYP-D3BJ/6-311++G(df,pd)                    | 4879.8        | -183.4     | 898.2        | 0.5         | 855.3        | 8.9         | 21.5     |
| B3LYP-D3BJ/6-311G(d,p)                        | 5183.1        | 119.9      | 889.8        | -7.9        | 835.0        | -11.4       | 21.5     |
| B3LYP-D3BJ/6-311+G(d,p)                       | 4887.8        | -175.4     | 894.8        | -2.9        | 851.4        | 5.0         | 23.2     |
| B3LYP-D3BJ/6-311++G(d,p)                      | 4890.1        | -173.1     | 894.8        | -2.9        | 851.2        | 4.8         | 15.2     |
| B3LYP-D3BJ/6-31G(d,p)                         | 4810.2        | -253.0     | 895.0        | -2.7        | 853.2        | 6.8         | 23.2     |
| <b>B3LYP-D3BJ/6-31+G(d,p)<sup>a</sup></b>     | <b>5063.8</b> | <b>0.6</b> | <b>895.6</b> | <b>-2.1</b> | <b>841.6</b> | <b>-4.8</b> | 20.1     |
| B3LYP-D3BJ/6-31++G(d,p)                       | 4808.5        | -254.7     | 895.0        | -2.7        | 853.4        | 7.0         | 20.3     |
| B3LYP-D3BJ/aug-cc-pVDZ                        | 4912.5        | -150.7     | 893.7        | -4.0        | 848.0        | 1.6         | 11.1     |
| B3LYP-D3BJ/aug-cc-pVTZ                        | 4953.8        | -109.4     | 896.1        | -1.6        | 851.1        | 4.7         | 16.5     |
| B3LYP-D3BJ/cc-pVDZ                            | 5204.8        | 141.6      | 890.0        | -7.7        | 832.1        | -14.3       | 8.6      |
| B3LYP-D3BJ/cc-pVTZ                            | 5089.3        | 26.1       | 893.1        | -4.6        | 843.2        | -3.2        | 13.3     |
| CCSD/cc-pVDZ                                  | 5200.6        | 137.4      | 888.1        | -9.6        | 830.1        | -16.3       | 10.7     |
| M06-2X/6-311G(3df,3pd)                        | 5307.2        | 244.0      | 904.6        | 6.9         | 843.8        | -2.6        | 9.7      |
| M06-2X/6-311+G(3df,3pd)                       | 5210.1        | 146.9      | 906.1        | 8.4         | 848.4        | 2.0         | 12.5     |
| M06-2X/6-311++G(3df,3pd)                      | 5205.7        | 142.5      | 906.3        | 8.6         | 848.7        | 2.3         | 12.6     |
| M06-2X/6-311G(df,pd)                          | 5299.8        | 236.6      | 904.3        | 6.6         | 843.2        | -3.2        | 9.5      |
| M06-2X/6-311+G(df,pd)                         | 5156.3        | 93.1       | 906.3        | 8.6         | 850.3        | 3.9         | 13.9     |
| M06-2X/6-311++G(df,pd)                        | 5145.4        | 82.2       | 906.7        | 9.0         | 851.0        | 4.6         | 14.2     |
| M06-2X/6-311G(d,p)                            | 5299.6        | 236.4      | 901.9        | 4.2         | 840.7        | -5.7        | 9.3      |
| M06-2X/6-311+G(d,p)                           | 5154.7        | 91.5       | 903.9        | 6.2         | 847.9        | 1.5         | 13.7     |

|                                      |               |               |              |             |              |             |      |
|--------------------------------------|---------------|---------------|--------------|-------------|--------------|-------------|------|
| M06-2X/6-311++G(d,p)                 | 5150.8        | 87.6          | 904.0        | 6.3         | 848.1        | 1.7         | 13.9 |
| M06-2X/6-31G(d,p)                    | 5232.3        | 169.1         | 905.7        | 8.0         | 843.9        | -2.5        | 10.2 |
| M06-2X/6-31+G(d,p)                   | 5130.1        | 66.9          | 902.9        | 5.2         | 846.6        | 0.2         | 13.9 |
| M06-2X/6-31++G(d,p)                  | 5127.4        | 64.2          | 903.0        | 5.3         | 846.8        | 0.4         | 14.0 |
| M06-2X/aug-cc-pVDZ                   | 5148.1        | 84.9          | 904.6        | 6.9         | 847.0        | 0.6         | 13.0 |
| M06-2X/aug-cc-pVTZ                   | 5200.4        | 137.2         | 905.1        | 7.4         | 848.2        | 1.8         | 12.9 |
| M06-2X/cc-pVDZ                       | 5297.8        | 234.6         | 903.6        | 5.9         | 840.0        | -6.4        | 8.2  |
| M06-2X/cc-pVTZ                       | 5262.1        | 198.9         | 904.1        | 6.4         | 845.1        | -1.3        | 11.1 |
| MP2/6-311G(3df,3pd)                  | 5069.1        | 5.9           | 916.2        | 18.5        | 859.5        | 13.1        | 15.3 |
| MP2/6-311+G(3df,3pd)                 | 4786.8        | -276.4        | 924.9        | 27.2        | 877.6        | 31.2        | 23.2 |
| MP2/6-311++G(3df,3pd)                | 4791.9        | -271.3        | 924.8        | 27.1        | 877.2        | 30.8        | 23.0 |
| MP2/6-311G(df,pd)                    | 4866.3        | -196.9        | 921.4        | 23.7        | 872.7        | 26.3        | 21.6 |
| MP2/6-311+G(df,pd)                   | 4432.1        | -631.1        | 940.3        | 42.6        | 904.3        | 57.9        | 33.5 |
| MP2/6-311++G(df,pd)                  | 4427.1        | -636.1        | 940.4        | 42.7        | 904.6        | 58.2        | 33.6 |
| MP2/6-311G(d,p)                      | 4846.6        | -216.6        | 913.3        | 15.6        | 865.3        | 18.9        | 21.4 |
| MP2/6-311+G(d,p)                     | 4410.8        | -652.4        | 932.4        | 34.7        | 897.2        | 50.8        | 33.4 |
| <b>MP2/6-311++G(d,p)<sup>b</sup></b> | <b>4407.0</b> | <b>-656.2</b> | <b>932.3</b> | <b>34.6</b> | <b>897.4</b> | <b>51.0</b> | 33.5 |
| MP2/6-31G(d,p)                       | 4975.9        | -87.3         | 909.2        | 11.5        | 855.4        | 9.0         | 17.3 |
| MP2/6-31+G(d,p)                      | 4509.8        | -553.4        | 923.8        | 26.1        | 886.4        | 40.0        | 30.5 |
| MP2/6-31++G(d,p)                     | 4365.4        | -697.8        | 931.2        | 33.5        | 897.9        | 51.5        | 34.6 |
| MP2/aug-cc-pVDZ                      | 4440.0        | -623.2        | 927.2        | 29.5        | 886.7        | 40.3        | 30.2 |
| MP2/aug-cc-pVTZ                      | 4761.7        | -301.5        | 924.5        | 26.8        | 877.4        | 31.0        | 23.6 |
| <b>MP2/cc-pVDZ<sup>a</sup></b>       | <b>5060.9</b> | <b>-2.3</b>   | <b>900.9</b> | <b>3.2</b>  | <b>844.0</b> | <b>-2.4</b> | 14.0 |
| MP2/cc-pVTZ                          | 4952.5        | -110.7        | 916.4        | 18.7        | 864.4        | 18.0        | 18.8 |
| <b>Expt.</b>                         | <b>5063.2</b> |               | <b>897.7</b> |             | <b>846.4</b> |             |      |

<sup>a</sup> Level of theory which has yielded rotational constants in best agreement with the experimental values.

<sup>b</sup> Our most frequently used level of theory.



**Table S-4.** The rotational constants  $A$ ,  $B$ ,  $C$  (in MHz) of conformer V of methyl valerate calculated at different levels of theory and their deviations to the experimental values (calc.–exp.)  $\Delta A$ ,  $\Delta B$ , and  $\Delta C$ , respectively (in MHz).

| <b>Basis set</b>                          | <b><math>A</math></b> | <b><math>\Delta A</math></b> | <b><math>B</math></b> | <b><math>\Delta B</math></b> | <b><math>C</math></b> | <b><math>\Delta C</math></b> |
|---|-----------------------|------------------------------|-----------------------|------------------------------|-----------------------|------------------------------|
| B3LYP-D3/6-311G(3df,3pd)                  | 7612.1                | 66.8                         | 737.6                 | -1.9                         | 686.6                 | -1.9                         |
| B3LYP-D3/6-311+G(3df,3pd)                 | 7611.3                | 66.0                         | 736.1                 | -3.4                         | 685.2                 | -3.3                         |
| B3LYP-D3/6-311++G(3df,3pd)                | 7611.5                | 66.2                         | 736.1                 | -3.4                         | 685.2                 | -3.3                         |
| B3LYP-D3/6-311G(df,pd)                    | 7593.4                | 48.1                         | 736.6                 | -2.9                         | 685.6                 | -2.9                         |
| B3LYP-D3/6-311+G(df,pd)                   | 7593.2                | 47.9                         | 734.9                 | -4.6                         | 684.1                 | -4.4                         |
| B3LYP-D3/6-311++G(df,pd)                  | 7593.3                | 48.0                         | 734.9                 | -4.6                         | 684.1                 | -4.4                         |
| B3LYP-D3/6-311G(d,p)                      | 7574.2                | 28.9                         | 734.6                 | -4.9                         | 683.8                 | -4.7                         |
| B3LYP-D3/6-311+G(d,p)                     | 7570.9                | 25.6                         | 732.9                 | -6.6                         | 682.3                 | -6.2                         |
| B3LYP-D3/6-311++G(d,p)                    | 7571.0                | 25.7                         | 732.9                 | -6.6                         | 682.3                 | -6.2                         |
| B3LYP-D3/6-31G(d,p)                       | 7534.1                | -11.2                        | 734.7                 | -4.8                         | 683.5                 | -5.0                         |
| B3LYP-D3/6-31+G(d,p)                      | 7531.2                | -14.1                        | 731.5                 | -8.0                         | 680.7                 | -7.8                         |
| B3LYP-D3/6-31++G(d,p)                     | 7531.5                | -13.8                        | 731.5                 | -8.0                         | 680.7                 | -7.8                         |
| B3LYP-D3/cc-pVDZ                          | 7523.4                | -21.9                        | 734.9                 | -4.6                         | 683.8                 | -4.7                         |
| B3LYP-D3/cc-pVTZ                          | 7599.2                | 53.9                         | 736.5                 | -3.0                         | 685.5                 | -3.0                         |
| B3LYP-D3/aug-cc-pVDZ                      | 7530.5                | -14.8                        | 732.6                 | -6.9                         | 681.8                 | -6.7                         |
| B3LYP-D3/aug-cc-pVTZ                      | 7600.2                | 54.9                         | 735.7                 | -3.8                         | 684.9                 | -3.6                         |
| B3LYP-D3BJ/6-311G(3df,3pd)                | 7622.1                | 76.8                         | 738.6                 | -0.9                         | 687.6                 | -0.9                         |
| B3LYP-D3BJ/6-311+G(3df,3pd)               | 7621.8                | 76.5                         | 737.2                 | -2.3                         | 686.3                 | -2.2                         |
| B3LYP-D3BJ/6-311++G(3df,3pd)              | 7622.0                | 76.7                         | 737.2                 | -2.3                         | 686.3                 | -2.2                         |
| B3LYP-D3BJ/6-311G(df,pd)                  | 7603.7                | 58.4                         | 737.6                 | -1.9                         | 686.6                 | -1.9                         |
| B3LYP-D3BJ/6-311+G(df,pd)                 | 7602.5                | 57.2                         | 735.8                 | -3.7                         | 685.0                 | -3.5                         |
| B3LYP-D3BJ/6-311++G(df,pd)                | 7602.6                | 57.3                         | 735.8                 | -3.7                         | 685.0                 | -3.5                         |
| B3LYP-D3BJ/6-311G(d,p)                    | 7584.1                | 38.8                         | 735.7                 | -3.8                         | 684.8                 | -3.7                         |
| B3LYP-D3BJ/6-311+G(d,p)                   | 7580.7                | 35.4                         | 734.0                 | -5.5                         | 683.2                 | -5.3                         |
| B3LYP-D3BJ/6-311++G(d,p)                  | 7580.9                | 35.6                         | 734.0                 | -5.5                         | 683.2                 | -5.3                         |
| B3LYP-D3BJ/6-31G(d,p)                     | 7541.7                | -3.6                         | 732.5                 | -7.0                         | 681.7                 | -6.8                         |
| <b>B3LYP-D3BJ/6-31+G(d,p)<sup>a</sup></b> | <b>7544.4</b>         | <b>-0.9</b>                  | <b>735.7</b>          | <b>-3.8</b>                  | <b>684.5</b>          | <b>-4.0</b>                  |
| B3LYP-D3BJ/6-31++G(d,p)                   | 7542.0                | -3.3                         | 732.5                 | -7.0                         | 681.7                 | -6.8                         |
| B3LYP-D3BJ/aug-cc-pVDZ                    | 7544.5                | -0.8                         | 733.5                 | -6.0                         | 682.7                 | -5.8                         |
| B3LYP-D3BJ/aug-cc-pVTZ                    | 7610.2                | 64.9                         | 736.8                 | -2.7                         | 685.9                 | -2.6                         |
| B3LYP-D3BJ/cc-pVDZ                        | 7534.3                | -11.0                        | 735.9                 | -3.6                         | 684.7                 | -3.8                         |
| B3LYP-D3BJ/cc-pVTZ                        | 7609.3                | 64.0                         | 737.6                 | -1.9                         | 686.5                 | -2.0                         |
| CCSD/cc-pVDZ                              | 7501.6                | -43.7                        | 735.0                 | -4.5                         | 683.8                 | -4.7                         |
| M06-2X/6-311G(3df,3pd)                    | 7676.5                | 131.2                        | 746.1                 | 6.6                          | 694.5                 | 6.0                          |
| M06-2X/6-311+G(3df,3pd)                   | 7677.2                | 131.9                        | 744.9                 | 5.4                          | 693.4                 | 4.9                          |
| M06-2X/6-311++G(3df,3pd)                  | 7677.3                | 132.0                        | 744.8                 | 5.3                          | 693.4                 | 4.9                          |
| M06-2X/6-311G(df,pd)                      | 7657.8                | 112.5                        | 745.0                 | 5.5                          | 693.4                 | 4.9                          |
| M06-2X/6-311+G(df,pd)                     | 7658.0                | 112.7                        | 743.7                 | 4.2                          | 692.3                 | 3.8                          |
| M06-2X/6-311G(d,p)                        | 7641.1                | 95.8                         | 743.6                 | 4.1                          | 692.1                 | 3.6                          |
| M06-2X/6-311+G(d,p)                       | 7640.9                | 95.6                         | 742.2                 | 2.7                          | 690.9                 | 2.4                          |
| M06-2X/6-311++G(d,p)                      | 7641.0                | 95.7                         | 742.2                 | 2.7                          | 690.9                 | 2.4                          |

|  |               |             |              |            |              |             |
|--|---------------|-------------|--------------|------------|--------------|-------------|
| M06-2X/6-31G(d,p)                      | 7608.1        | 62.8        | 743.7        | 4.2        | 691.9        | 3.4         |
| M06-2X/6-31+G(d,p)                     | 7606.0        | 60.7        | 741.0        | 1.5        | 689.6        | 1.1         |
| M06-2X/6-31++G(d,p)                    | 7606.5        | 61.2        | 741.0        | 1.5        | 689.6        | 1.1         |
| M06-2X/aug-cc-pVDZ                     | 7609.7        | 64.4        | 742.2        | 2.7        | 690.7        | 2.2         |
| M06-2X/aug-cc-pVTZ                     | 7667.7        | 122.4       | 744.6        | 5.1        | 693.1        | 4.6         |
| M06-2X/cc-pVDZ                         | 7603.3        | 58.0        | 744.4        | 4.9        | 692.6        | 4.1         |
| M06-2X/cc-pVTZ                         | 7665.4        | 120.1       | 745.2        | 5.7        | 693.6        | 5.1         |
| MP2/6-311G(3df,3pd)                    | 7598.4        | 53.1        | 747.8        | 8.3        | 695.3        | 6.8         |
| MP2/6-311+G(3df,3pd)                   | 7597.6        | 52.3        | 746.0        | 6.5        | 693.8        | 5.3         |
| MP2/6-311++G(3df,3pd)                  | 7597.5        | 52.2        | 746.0        | 6.5        | 693.8        | 5.3         |
| MP2/6-311G(df,pd)                      | 7596.8        | 51.5        | 746.7        | 7.2        | 694.4        | 5.9         |
| MP2/6-311+G(df,pd)                     | 7592.1        | 46.8        | 744.7        | 5.2        | 692.7        | 4.2         |
| MP2/6-311++G(df,pd)                    | 7591.6        | 46.3        | 744.7        | 5.2        | 692.7        | 4.2         |
| <b>MP2/6-311G(d,p)<sup>a</sup></b>     | <b>7544.0</b> | <b>-1.3</b> | <b>741.4</b> | <b>1.9</b> | <b>689.4</b> | <b>0.9</b>  |
| <b>MP2/6-311+G(d,p)<sup>a</sup></b>    | <b>7537.1</b> | <b>-8.2</b> | <b>739.8</b> | <b>0.3</b> | <b>688.0</b> | <b>-0.5</b> |
| <b>MP2/6-311++G(d,p)<sup>a,b</sup></b> | <b>7537.1</b> | <b>-8.2</b> | <b>739.8</b> | <b>0.3</b> | <b>688.0</b> | <b>-0.5</b> |
| MP2/6-31G(d,p)                         | 7518.6        | -26.7       | 741.8        | 2.3        | 689.5        | 1.0         |
| MP2/6-31+G(d,p)                        | 7503.0        | -42.3       | 738.9        | -0.6       | 686.9        | -1.6        |
| MP2/6-31++G(d,p)                       | 7502.2        | -43.1       | 738.8        | -0.7       | 686.8        | -1.7        |
| MP2/aug-cc-pVDZ                        | 7452.3        | -93.0       | 735.1        | -4.4       | 683.5        | -5.0        |
| MP2/aug-cc-pVTZ                        | 7573.8        | 28.5        | 745.2        | 5.7        | 692.9        | 4.4         |
| MP2/cc-pVDZ                            | 7473.5        | -71.8       | 738.8        | -0.7       | 686.8        | -1.7        |
| MP2/cc-pVTZ                            | 7582.3        | 37.0        | 746.1        | 6.6        | 693.7        | 5.2         |
| <b>Expt.</b>                           | <b>7545.3</b> |             | <b>739.5</b> |            | <b>688.5</b> |             |

<sup>a</sup> Level of theory which has yielded rotational constants in best agreement with the experimental values.

<sup>b</sup> Our most frequently used level of theory.

**Table S-5.** Observed 85 A and 83 E species frequencies ( $\nu_{\text{Obs.}}$ ) of conformer I of methyl valerate.  $\nu_{\text{Obs.}} - \nu_{\text{Calc.}}$  values as obtained with the program *XIAM*.

| $J$         | $K_a$ | $K_c$ | $J$         | $K_a$ | $K_c$ |   | $\nu_{\text{Obs.}}$ | $\nu_{\text{Obs.}} - \nu_{\text{Calc.}}$ |
|-------------|-------|-------|-------------|-------|-------|---|---------------------|--|
| upper level |       |       | lower level |       |       |   | GHz                 | kHz                                      |
| 4           | 0     | 4     | 3           | 0     | 3     | A | 6.9719293           | -1.3                                     |
| 4           | 0     | 4     | 3           | 0     | 3     | E | 6.9719052           | 2.0                                      |
| 4           | 1     | 4     | 3           | 1     | 3     | A | 6.8731872           | -2.8                                     |
| 4           | 1     | 4     | 3           | 1     | 3     | E | 6.8732613           | 4.4                                      |
| 4           | 1     | 3     | 3           | 1     | 2     | A | 7.0783014           | -1.3                                     |
| 4           | 1     | 3     | 3           | 1     | 2     | E | 7.0781827           | 0.6                                      |
| 4           | 2     | 3     | 3           | 2     | 2     | A | 6.9764833           | 0.0                                      |
| 4           | 2     | 3     | 3           | 2     | 2     | E | 6.9784659           | 1.9                                      |
| 4           | 2     | 2     | 3           | 2     | 1     | A | 6.9811830           | -1.9                                     |
| 4           | 2     | 2     | 3           | 2     | 1     | E | 6.9791513           | 2.0                                      |
| 4           | 3     | 1     | 3           | 3     | 0     | A | 6.9780682           | 2.2                                      |
| 4           | 3     | 1     | 3           | 3     | 0     | E | 6.9780259           | -2.0                                     |
| 5           | 0     | 5     | 4           | 0     | 4     | A | 8.7113431           | -1.8                                     |
| 5           | 0     | 5     | 4           | 0     | 4     | E | 8.7113136           | 2.3                                      |
| 5           | 1     | 5     | 4           | 1     | 4     | A | 8.5905702           | -1.6                                     |
| 5           | 1     | 5     | 4           | 1     | 4     | E | 8.5905988           | 3.7                                      |
| 5           | 1     | 4     | 4           | 1     | 3     | A | 8.8469320           | -1.3                                     |
| 5           | 1     | 4     | 4           | 1     | 3     | E | 8.8468439           | 0.9                                      |
| 5           | 2     | 4     | 4           | 2     | 3     | A | 8.7199672           | -1.5                                     |
| 5           | 2     | 4     | 4           | 2     | 3     | E | 8.7230108           | 2.3                                      |
| 5           | 2     | 3     | 4           | 2     | 2     | A | 8.7293625           | -2.1                                     |
| 5           | 2     | 3     | 4           | 2     | 2     | E | 8.7262580           | 2.3                                      |
| 5           | 3     | 3     | 4           | 3     | 2     | A | 8.7229366           | -0.8                                     |
| 5           | 3     | 3     | 4           | 3     | 2     | E | 8.7229345           | -1.3                                     |
| 6           | 0     | 6     | 5           | 0     | 5     | A | 10.4483938          | -2.4                                     |
| 6           | 0     | 6     | 5           | 0     | 5     | E | 10.4483604          | 3.5                                      |
| 6           | 1     | 6     | 5           | 1     | 5     | A | 10.3073542          | -3.5                                     |
| 6           | 1     | 6     | 5           | 1     | 5     | E | 10.3073654          | 4.8                                      |
| 6           | 1     | 5     | 5           | 1     | 4     | A | 10.6149167          | -2.0                                     |
| 6           | 1     | 5     | 5           | 1     | 4     | E | 10.6148369          | 1.1                                      |
| 6           | 2     | 5     | 5           | 2     | 4     | A | 10.4630287          | -1.8                                     |
| 6           | 2     | 5     | 5           | 2     | 4     | E | 10.4662116          | 4.3                                      |
| 6           | 2     | 4     | 5           | 2     | 3     | A | 10.4794486          | -1.9                                     |
| 6           | 2     | 4     | 5           | 2     | 3     | E | 10.4761904          | 0.3                                      |
| 6           | 3     | 4     | 5           | 3     | 4     | E | 10.4681030          | 2.9                                      |
| 7           | 0     | 7     | 6           | 0     | 6     | A | 12.1826363          | -2.6                                     |
| 7           | 0     | 7     | 6           | 0     | 6     | E | 12.1825982          | 3.7                                      |
| 7           | 1     | 7     | 6           | 1     | 6     | A | 12.0234394          | -3.6                                     |
| 7           | 1     | 6     | 6           | 1     | 5     | A | 12.3821147          | -0.1                                     |
| 7           | 1     | 6     | 6           | 1     | 5     | E | 12.3820313          | 0.5                                      |
| 7           | 2     | 6     | 6           | 2     | 5     | A | 12.2055819          | -1.9                                     |

Table S-5. continued

| <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> |   | <i>V</i> <sub>Obs.</sub> | <i>V</i> <sub>Obs.</sub> - <i>V</i> <sub>Calc.</sub> |
|-------------|----------------------|----------------------|-------------|----------------------|----------------------|---|--------------------------|--|
| upper level |                      |                      | lower level |                      |                      |   | GHz                      | kHz  |
| 7           | 2                    | 6                    | 6           | 2                    | 5                    | E | 12.2079333               | 4.5  |
| 7           | 2                    | 5                    | 6           | 2                    | 4                    | A | 12.2317942               | -2.4   |
| 7           | 2                    | 5                    | 6           | 2                    | 4                    | E | 12.2293548               | 1.3  |
| 7           | 3                    | 5                    | 6           | 3                    | 4                    | A | 12.2134506               | -1.1   |
| 7           | 3                    | 5                    | 6           | 3                    | 4                    | E | 12.2135760               | -2.8   |
| 7           | 3                    | 4                    | 6           | 3                    | 3                    | A | 12.2137957               | 4.7  |
| 8           | 0                    | 8                    | 7           | 0                    | 7                    | A | 13.9136528               | -3.2   |
| 8           | 0                    | 8                    | 7           | 0                    | 7                    | E | 13.9136114               | 4.3  |
| 8           | 1                    | 8                    | 7           | 1                    | 7                    | A | 13.7387281               | -2.4   |
| 8           | 1                    | 8                    | 7           | 1                    | 7                    | E | 13.7387177               | 3.8  |
| 8           | 1                    | 7                    | 7           | 1                    | 6                    | A | 14.1483673               | -1.8   |
| 8           | 1                    | 7                    | 7           | 1                    | 6                    | E | 14.1482824               | 2.3  |
| 8           | 2                    | 7                    | 7           | 2                    | 6                    | A | 13.9475424               | -2.4   |
| 8           | 2                    | 7                    | 7           | 2                    | 6                    | E | 13.9489709               | 7.2  |
| 8           | 2                    | 6                    | 7           | 2                    | 5                    | A | 13.9867253               | -2.8   |
| 8           | 2                    | 6                    | 7           | 2                    | 5                    | E | 13.9851944               | -1.4   |
| 9           | 0                    | 9                    | 8           | 0                    | 8                    | A | 15.6410690               | -4.7   |
| 9           | 0                    | 9                    | 8           | 0                    | 8                    | E | 15.6410269               | 5.9  |
| 9           | 1                    | 9                    | 8           | 1                    | 8                    | A | 15.4531290               | -2.8   |
| 9           | 1                    | 9                    | 8           | 1                    | 8                    | E | 15.4531135               | 3.8  |
| 9           | 1                    | 8                    | 8           | 1                    | 7                    | A | 15.9135175               | -1.7   |
| 9           | 1                    | 8                    | 8           | 1                    | 7                    | E | 15.9134258               | 2.2  |
| 9           | 2                    | 8                    | 8           | 2                    | 7                    | A | 15.6888254               | -3.4   |
| 9           | 2                    | 8                    | 8           | 2                    | 7                    | E | 15.6896402               | 4.4  |
| 9           | 2                    | 7                    | 8           | 2                    | 6                    | A | 15.7445233               | -3.1   |
| 9           | 2                    | 7                    | 8           | 2                    | 6                    | E | 15.7435927               | 2.2  |
| 3           | 2                    | 2                    | 3           | 1                    | 2                    | A | 12.4196445               | -4.7   |
| 4           | 2                    | 3                    | 4           | 1                    | 3                    | A | 12.3178279               | -2.0   |
| 4           | 2                    | 3                    | 4           | 1                    | 3                    | E | 12.3040688               | 0.0  |
| 5           | 2                    | 4                    | 5           | 1                    | 4                    | A | 12.1908646               | -0.8   |
| 5           | 2                    | 4                    | 5           | 1                    | 4                    | E | 12.1802370               | 2.7  |
| 6           | 2                    | 5                    | 6           | 1                    | 5                    | A | 12.0389768               | -0.3   |
| 6           | 2                    | 5                    | 6           | 1                    | 5                    | E | 12.0316066               | 0.7  |
| 7           | 2                    | 6                    | 7           | 1                    | 6                    | A | 11.8624465               | 0.3  |
| 7           | 2                    | 6                    | 7           | 1                    | 6                    | E | 11.8574963               | -7.7   |
| 8           | 2                    | 7                    | 8           | 1                    | 7                    | A | 11.6616188               | -3.0   |
| 8           | 2                    | 7                    | 8           | 1                    | 7                    | E | 11.6581894               | 1.9  |
| 9           | 2                    | 8                    | 9           | 1                    | 8                    | A | 11.4369289               | -2.5   |
| 9           | 2                    | 8                    | 9           | 1                    | 8                    | E | 11.4344025               | 2.7  |
| 1           | 1                    | 0                    | 0           | 0                    | 0                    | A | 5.9610860                | -1.6   |
| 1           | 1                    | 0                    | 0           | 0                    | 0                    | E | 5.9619031                | -0.2   |
| 2           | 1                    | 1                    | 1           | 0                    | 1                    | A | 7.7565640                | 1.0  |
| 2           | 1                    | 1                    | 1           | 0                    | 1                    | E | 7.7565873                | 3.1  |

Table S-5. continued

| <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> |   | <i>V</i> <sub>Obs.</sub> | <i>V</i> <sub>Obs.</sub> - <i>V</i> <sub>Calc.</sub> |
|-------------|----------------------|----------------------|-------------|----------------------|----------------------|---|--------------------------|--|
| upper level |                      |                      | lower level |                      |                      |   | GHz                      | kHz  |
| 3           | 1                    | 2                    | 2           | 0                    | 2                    | A | 9.5778532                | -2.0   |
| 3           | 1                    | 2                    | 2           | 0                    | 2                    | E | 9.5776603                | 0.6  |
| 4           | 1                    | 3                    | 3           | 0                    | 3                    | A | 11.4255415               | -0.7   |
| 4           | 1                    | 3                    | 3           | 0                    | 3                    | E | 11.4252476               | 0.7  |
| 5           | 1                    | 4                    | 4           | 0                    | 4                    | A | 13.3005410               | -3.8   |
| 5           | 1                    | 4                    | 4           | 0                    | 4                    | E | 13.3001881               | 1.3  |
| 6           | 1                    | 5                    | 5           | 0                    | 5                    | A | 15.2041168               | -1.8   |
| 6           | 1                    | 5                    | 5           | 0                    | 5                    | E | 15.2037108               | -0.6   |
| 7           | 1                    | 6                    | 6           | 0                    | 6                    | A | 17.1378349               | -2.4   |
| 7           | 1                    | 6                    | 6           | 0                    | 6                    | E | 17.1373834               | -1.8   |
| 8           | 1                    | 7                    | 7           | 0                    | 7                    | A | 19.1035645               | -2.9   |
| 8           | 1                    | 7                    | 7           | 0                    | 7                    | E | 19.1030697               | -1.1   |
| 9           | 1                    | 8                    | 8           | 0                    | 8                    | A | 21.1034307               | 0.0  |
| 9           | 1                    | 8                    | 8           | 0                    | 8                    | E | 21.1028868               | -0.5   |
| 2           | 2                    | 0                    | 2           | 1                    | 2                    | E | 12.6652851               | -4.5   |
| 3           | 2                    | 1                    | 3           | 1                    | 3                    | A | 12.7296881               | 5.8  |
| 3           | 2                    | 1                    | 3           | 1                    | 3                    | E | 12.7433986               | 4.0  |
| 4           | 2                    | 2                    | 4           | 1                    | 4                    | A | 12.8376830               | 5.8  |
| 4           | 2                    | 2                    | 4           | 1                    | 4                    | E | 12.8492816               | -5.3   |
| 5           | 2                    | 3                    | 5           | 1                    | 5                    | A | 12.9764753               | 5.3  |
| 5           | 2                    | 3                    | 5           | 1                    | 5                    | E | 12.9849522               | 4.7  |
| 6           | 2                    | 4                    | 6           | 1                    | 6                    | A | 13.1485631               | 0.3  |
| 6           | 2                    | 4                    | 6           | 1                    | 6                    | E | 13.1537777               | 0.7  |
| 8           | 2                    | 6                    | 8           | 1                    | 8                    | A | 13.6049141               | 0.0  |
| 8           | 2                    | 6                    | 8           | 1                    | 8                    | E | 13.6061795               | 1.3  |
| 9           | 2                    | 7                    | 9           | 1                    | 9                    | A | 13.8963101               | 1.5  |
| 9           | 2                    | 7                    | 9           | 1                    | 9                    | E | 13.8966608               | 1.8  |
| 9           | 0                    | 9                    | 8           | 1                    | 7                    | A | 10.4511570               | -5.3   |
| 9           | 0                    | 9                    | 8           | 1                    | 7                    | E | 10.4515656               | 8.3  |
| 2           | 2                    | 0                    | 2           | 1                    | 1                    | A | 12.4966296               | 4.8  |
| 2           | 2                    | 0                    | 2           | 1                    | 1                    | E | 12.5106670               | 3.9  |
| 3           | 2                    | 1                    | 3           | 1                    | 2                    | A | 12.4220031               | 2.2  |
| 3           | 2                    | 1                    | 3           | 1                    | 2                    | E | 12.4353483               | -0.7   |
| 4           | 2                    | 2                    | 4           | 1                    | 3                    | A | 12.3248829               | -0.1   |
| 5           | 2                    | 3                    | 5           | 1                    | 4                    | A | 12.2073131               | -1.2   |
| 5           | 2                    | 3                    | 5           | 1                    | 4                    | E | 12.2157254               | -3.5   |
| 6           | 2                    | 4                    | 6           | 1                    | 5                    | A | 12.0718435               | -2.6   |
| 6           | 2                    | 4                    | 6           | 1                    | 5                    | E | 12.0770762               | -6.9   |
| 7           | 2                    | 5                    | 7           | 1                    | 6                    | A | 11.9215278               | -0.1   |
| 7           | 2                    | 5                    | 7           | 1                    | 6                    | E | 11.9244054               | -0.5   |
| 8           | 2                    | 6                    | 8           | 1                    | 7                    | A | 11.7598852               | -1.7   |
| 8           | 2                    | 6                    | 8           | 1                    | 7                    | E | 11.7613237               | 2.2  |
| 9           | 2                    | 7                    | 9           | 1                    | 8                    | A | 11.5908946               | 0.6  |

Table S-5. continued

| <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> |   | <i>V</i> <sub>Obs.</sub> | <i>V</i> <sub>Obs.</sub> - <i>V</i> <sub>Calc.</sub> |
|-------------|----------------------|----------------------|-------------|----------------------|----------------------|---|--------------------------|--|
| upper level |                      |                      | lower level |                      |                      |   | GHz                      | kHz  |
| 2           | 2                    | 1                    | 2           | 1                    | 2                    | A | 12.6499938               | -1.3   |
| 2           | 2                    | 1                    | 2           | 1                    | 2                    | E | 12.6338116               | 4.3  |
| 3           | 2                    | 2                    | 3           | 1                    | 3                    | A | 12.7273283               | -2.4   |
| 3           | 2                    | 2                    | 3           | 1                    | 3                    | E | 12.7118360               | 3.5  |
| 4           | 2                    | 3                    | 4           | 1                    | 4                    | A | 12.8306192               | -4.9   |
| 4           | 2                    | 3                    | 4           | 1                    | 4                    | E | 12.8170392               | -0.4   |
| 5           | 2                    | 4                    | 5           | 1                    | 5                    | A | 12.9600223               | 1.3  |
| 5           | 2                    | 4                    | 5           | 1                    | 5                    | E | 12.9494505               | -2.4   |
| 6           | 2                    | 5                    | 6           | 1                    | 6                    | A | 13.1156971               | 3.3  |
| 6           | 2                    | 5                    | 6           | 1                    | 6                    | E | 13.1082916               | -8.1   |
| 7           | 2                    | 6                    | 7           | 1                    | 7                    | A | 13.2978359               | 1.2  |
| 7           | 2                    | 6                    | 7           | 1                    | 7                    | E | 13.2927914               | -3.0   |
| 8           | 2                    | 7                    | 8           | 1                    | 8                    | A | 13.5066523               | 3.2  |
| 8           | 2                    | 7                    | 8           | 1                    | 8                    | E | 13.5030408               | -3.4   |
| 9           | 2                    | 8                    | 9           | 1                    | 9                    | A | 13.7423485               | 2.5  |
| 9           | 2                    | 8                    | 9           | 1                    | 9                    | E | 13.7395722               | 1.9  |
| 1           | 1                    | 1                    | 0           | 0                    | 0                    | E | 5.9082640                | 2.2  |
| 2           | 1                    | 2                    | 1           | 0                    | 1                    | A | 7.6027190                | -3.2   |
| 2           | 1                    | 2                    | 1           | 0                    | 1                    | E | 7.6019580                | 0.1  |
| 3           | 1                    | 3                    | 2           | 0                    | 2                    | A | 9.2701726                | -1.2   |
| 3           | 1                    | 3                    | 2           | 0                    | 2                    | E | 9.2696168                | 2.6  |
| 4           | 1                    | 4                    | 3           | 0                    | 3                    | A | 10.9127444               | -3.6   |
| 4           | 1                    | 4                    | 3           | 0                    | 3                    | E | 10.9122808               | 4.6  |
| 5           | 1                    | 5                    | 4           | 0                    | 4                    | A | 12.5313855               | -3.6   |
| 5           | 1                    | 5                    | 4           | 0                    | 4                    | E | 12.5309735               | 5.3  |
| 6           | 1                    | 6                    | 5           | 0                    | 5                    | A | 14.1273981               | -3.8   |
| 6           | 1                    | 6                    | 5           | 0                    | 5                    | E | 14.1270235               | 6.0  |
| 7           | 1                    | 7                    | 6           | 0                    | 6                    | A | 15.7024453               | -3.4   |
| 7           | 1                    | 7                    | 6           | 0                    | 6                    | E | 15.7020946               | -0.1   |
| 8           | 1                    | 8                    | 7           | 0                    | 7                    | A | 17.2585352               | -5.1   |
| 8           | 1                    | 8                    | 7           | 0                    | 7                    | E | 17.2582208               | 6.6  |
| 9           | 1                    | 9                    | 8           | 0                    | 8                    | A | 18.7980088               | -7.2   |
| 9           | 1                    | 9                    | 8           | 0                    | 8                    | E | 18.7977258               | 9.1  |
| 6           | 0                    | 6                    | 5           | 1                    | 5                    | A | 6.6283483                | -3.7   |
| 6           | 0                    | 6                    | 5           | 1                    | 5                    | E | 6.6286985                | -1.5   |
| 7           | 0                    | 7                    | 6           | 1                    | 6                    | A | 8.5036328                | -0.4   |
| 7           | 0                    | 7                    | 6           | 1                    | 6                    | E | 8.5039352                | 1.2  |
| 8           | 0                    | 8                    | 7           | 1                    | 7                    | A | 10.3938447               | -1.6   |
| 8           | 0                    | 8                    | 7           | 1                    | 7                    | E | 10.3941068               | -0.2   |
| 9           | 0                    | 9                    | 8           | 1                    | 8                    | A | 12.2961883               | -1.2   |
| 9           | 0                    | 9                    | 8           | 1                    | 8                    | E | 12.2964110               | -3.0   |

**Table S-6.** Observed 52 A and 52 E species frequencies ( $\nu_{\text{Obs.}}$ ) of conformer V of methyl valerate.  $\nu_{\text{Obs.}} - \nu_{\text{Calc.}}$  values as obtained with the program *XIAM*.

| $J \quad K_a \quad K_c$ |   |   | $J \quad K_a \quad K_c$ |   |   |   | $\nu_{\text{Obs.}}$ | $\nu_{\text{Obs.}} - \nu_{\text{Calc.}}$ |
|-------------------------|---|---|-------------------------|---|---|---|---------------------|--|
| upper level             |   |   | lower level             |   |   |   | GHz                 | <i>XIAM</i> / kHz                        |
| 1                       | 1 | 1 | 0                       | 0 | 0 | A | 8.2346574           | -3.5                                     |
| 1                       | 1 | 1 | 0                       | 0 | 0 | E | 8.2291884           | -1.0                                     |
| 1                       | 1 | 0 | 1                       | 0 | 1 | A | 6.8576024           | 5.5                                      |
| 1                       | 1 | 0 | 1                       | 0 | 1 | E | 6.8606277           | 0.5                                      |
| 2                       | 1 | 2 | 1                       | 0 | 1 | A | 9.6117206           | -3.3                                     |
| 2                       | 1 | 2 | 1                       | 0 | 1 | E | 9.6089916           | 8.2                                      |
| 2                       | 2 | 0 | 1                       | 1 | 0 | E | 23.3496011          | -3.6                                     |
| 2                       | 2 | 1 | 1                       | 1 | 0 | A | 23.3268604          | -1.5                                     |
| 2                       | 2 | 1 | 1                       | 1 | 1 | E | 23.348032           | -3.6                                     |
| 2                       | 1 | 1 | 2                       | 0 | 2 | A | 6.9088099           | -8.3                                     |
| 2                       | 1 | 1 | 2                       | 0 | 2 | E | 6.9091085           | -7.3                                     |
| 3                       | 1 | 3 | 2                       | 0 | 2 | A | 10.9634233          | -1.4                                     |
| 3                       | 1 | 3 | 2                       | 0 | 2 | E | 10.9614436          | 3.8                                      |
| 3                       | 1 | 2 | 3                       | 0 | 3 | A | 6.9861801           | -3.5                                     |
| 3                       | 1 | 2 | 3                       | 0 | 3 | E | 6.985724            | 0.0                                      |
| 4                       | 1 | 4 | 3                       | 0 | 3 | A | 12.2901185          | -2.4                                     |
| 4                       | 1 | 4 | 3                       | 0 | 3 | E | 12.2884424          | -1.6                                     |
| 4                       | 1 | 3 | 4                       | 0 | 4 | A | 7.0903292           | -2.2                                     |
| 4                       | 1 | 3 | 4                       | 0 | 4 | E | 7.0895618           | -0.6                                     |
| 4                       | 2 | 2 | 4                       | 1 | 3 | A | 20.2464364          | -2.7                                     |
| 4                       | 2 | 2 | 4                       | 1 | 3 | E | 20.2707749          | -4.2                                     |
| 4                       | 2 | 3 | 4                       | 1 | 4 | A | 20.7515339          | 3.1                                      |
| 4                       | 2 | 3 | 4                       | 1 | 4 | E | 20.7198937          | -0.7                                     |
| 4                       | 3 | 2 | 4                       | 2 | 3 | A | 34.1613183          | -5.7                                     |
| 4                       | 3 | 2 | 4                       | 2 | 3 | E | 34.1383044          | 14.8                                     |
| 5                       | 1 | 5 | 4                       | 0 | 4 | A | 13.5923835          | -2.9                                     |
| 5                       | 1 | 5 | 4                       | 0 | 4 | E | 13.5908656          | -0.8                                     |
| 5                       | 2 | 4 | 4                       | 1 | 3 | A | 27.3815307          | 4.5                                      |
| 5                       | 2 | 4 | 4                       | 1 | 3 | E | 27.3515072          | 5.5                                      |
| 5                       | 1 | 4 | 5                       | 0 | 5 | A | 7.222108            | -1.0                                     |
| 5                       | 1 | 4 | 5                       | 0 | 5 | E | 7.2211824           | 0.1                                      |
| 5                       | 2 | 3 | 5                       | 1 | 4 | A | 20.1254116          | 1.6                                      |
| 5                       | 2 | 3 | 5                       | 1 | 4 | E | 20.1473862          | -1.6                                     |
| 5                       | 2 | 4 | 5                       | 1 | 4 | E | 20.0855931          | 3.8                                      |
| 5                       | 2 | 4 | 5                       | 1 | 5 | A | 20.8794702          | -0.9                                     |
| 5                       | 2 | 4 | 5                       | 1 | 5 | E | 20.8502026          | 4.9                                      |
| 5                       | 3 | 2 | 5                       | 2 | 3 | A | 34.1529812          | 0.4                                      |
| 5                       | 3 | 2 | 5                       | 2 | 3 | E | 34.1664275          | -3.2                                     |
| 5                       | 3 | 3 | 5                       | 2 | 4 | A | 34.1629178          | -0.4                                     |
| 5                       | 3 | 3 | 5                       | 2 | 4 | E | 34.1373745          | -1.0                                     |
| 5                       | 2 | 3 | 6                       | 1 | 6 | A | 12.4765015          | -4.8                                     |

Table S-6. continued

| <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> |   | <i>V</i> <sub>Obs.</sub> | <i>V</i> <sub>Obs.</sub> - <i>V</i> <sub>Calc.</sub> |
|-------------|----------------------|----------------------|-------------|----------------------|----------------------|---|--------------------------|--|
| upper level |                      |                      | lower level |                      |                      |   | GHz                      | kHz  |
| 6           | 1                    | 6                    | 5           | 0                    | 5                    | A | 14.8710093               | -3.3   |
| 6           | 1                    | 6                    | 5           | 0                    | 5                    | E | 14.869586                | 0.8  |
| 6           | 2                    | 4                    | 5           | 1                    | 5                    | A | 29.4661039               | 5.1  |
| 6           | 2                    | 4                    | 5           | 1                    | 5                    | E | 29.4848491               | 6.3  |
| 6           | 2                    | 5                    | 5           | 1                    | 4                    | A | 28.6821486               | 0.1  |
| 6           | 2                    | 5                    | 5           | 1                    | 4                    | E | 28.656086                | 1.4  |
| 6           | 1                    | 5                    | 6           | 0                    | 6                    | A | 7.3825713                | 2.0  |
| 6           | 1                    | 5                    | 6           | 0                    | 6                    | E | 7.3815501                | 0.3  |
| 6           | 2                    | 4                    | 6           | 1                    | 5                    | A | 19.9835774               | -0.9   |
| 6           | 2                    | 4                    | 6           | 1                    | 5                    | E | 20.0018466               | -0.5   |
| 6           | 2                    | 5                    | 6           | 1                    | 5                    | E | 19.9376954               | -2.0   |
| 6           | 2                    | 5                    | 6           | 1                    | 6                    | A | 21.0332413               | -3.5   |
| 6           | 2                    | 5                    | 6           | 1                    | 6                    | E | 21.0076838               | 2.1  |
| 6           | 3                    | 3                    | 6           | 2                    | 4                    | A | 34.1458923               | 2.8  |
| 6           | 3                    | 3                    | 6           | 2                    | 4                    | E | 34.1631125               | 0.3  |
| 6           | 3                    | 4                    | 6           | 2                    | 5                    | A | 34.1657301               | 0.3  |
| 6           | 3                    | 4                    | 6           | 2                    | 5                    | E | 34.1364154               | 1.0  |
| 6           | 2                    | 5                    | 7           | 1                    | 6                    | A | 9.7932033                | 8.1  |
| 7           | 1                    | 7                    | 6           | 0                    | 6                    | A | 16.1270041               | -4.3   |
| 7           | 1                    | 7                    | 6           | 0                    | 6                    | E | 16.1256431               | 1.0  |
| 7           | 2                    | 5                    | 6           | 1                    | 6                    | A | 31.0628453               | -5.2   |
| 7           | 2                    | 5                    | 6           | 1                    | 6                    | E | 31.0768197               | -2.8   |
| 7           | 1                    | 6                    | 7           | 0                    | 7                    | A | 7.5729649                | 1.0  |
| 7           | 1                    | 6                    | 7           | 0                    | 7                    | E | 7.5718839                | 0.2  |
| 7           | 2                    | 5                    | 7           | 1                    | 6                    | A | 19.8227999               | -0.9   |
| 7           | 2                    | 5                    | 7           | 1                    | 6                    | E | 19.8364544               | -1.9   |
| 7           | 2                    | 6                    | 7           | 1                    | 7                    | A | 21.2129794               | 2.5  |
| 7           | 2                    | 6                    | 7           | 1                    | 7                    | E | 21.192025                | -4.2   |
| 7           | 3                    | 4                    | 7           | 2                    | 5                    | A | 34.1346053               | 0.5  |
| 7           | 3                    | 5                    | 7           | 2                    | 6                    | A | 34.1702384               | -1.4   |
| 7           | 3                    | 5                    | 7           | 2                    | 6                    | E | 34.1363141               | -0.3   |
| 7           | 4                    | 4                    | 8           | 3                    | 5                    | A | 36.3940636               | -0.7   |
| 8           | 0                    | 8                    | 7           | 1                    | 7                    | A | 5.2531768                | -4.2   |
| 8           | 0                    | 8                    | 7           | 1                    | 7                    | E | 5.2545159                | 4.9  |
| 8           | 1                    | 8                    | 7           | 0                    | 7                    | A | 17.3615981               | -1.4   |
| 8           | 1                    | 8                    | 7           | 0                    | 7                    | E | 17.360277                | -0.7   |
| 8           | 1                    | 7                    | 8           | 0                    | 8                    | A | 7.7947391                | 5.6  |
| 8           | 1                    | 7                    | 8           | 0                    | 8                    | E | 7.7936096                | -0.8   |
| 8           | 2                    | 6                    | 8           | 1                    | 7                    | A | 19.6452383               | -1.2   |
| 8           | 2                    | 6                    | 8           | 1                    | 7                    | E | 19.6543117               | 2.1  |
| 8           | 2                    | 7                    | 8           | 1                    | 8                    | A | 21.4188006               | -5.0   |
| 8           | 2                    | 7                    | 8           | 1                    | 8                    | E | 21.4024444               | -1.9   |
| 8           | 3                    | 5                    | 8           | 2                    | 6                    | A | 34.1177744               | 5.5  |



Table S-6. continued

| <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> | <i>J</i>    | <i>K<sub>a</sub></i> | <i>K<sub>c</sub></i> |   | <i>v</i> <sub>Obs.</sub> | <i>v</i> <sub>Obs.</sub> - <i>v</i> <sub>Calc.</sub> |
|-------------|----------------------|----------------------|-------------|----------------------|----------------------|---|--------------------------|--|
| upper level |                      |                      | lower level |                      |                      |   | GHz                      | kHz  |
| 8           | 3                    | 5                    | 8           | 2                    | 6                    | E | 34.1441011               | -2.2   |
| 8           | 3                    | 6                    | 8           | 2                    | 6                    | E | 34.0532699               | -3.3   |
| 8           | 3                    | 6                    | 8           | 2                    | 7                    | A | 34.1770063               | 4.4  |
| 8           | 3                    | 6                    | 8           | 2                    | 7                    | E | 34.1385722               | -2.4   |
| 8           | 4                    | 5                    | 9           | 3                    | 6                    | A | 34.9630766               | -3.0   |
| 9           | 0                    | 9                    | 8           | 1                    | 8                    | A | 6.8564779                | -1.0   |
| 9           | 0                    | 9                    | 8           | 1                    | 8                    | E | 6.8577666                | 8.1  |
| 9           | 1                    | 9                    | 8           | 0                    | 8                    | A | 18.5762211               | -4.0   |
| 9           | 1                    | 9                    | 8           | 0                    | 8                    | E | 18.5749365               | -1.8   |
| 9           | 1                    | 8                    | 9           | 0                    | 9                    | A | 8.0494922                | -2.0   |
| 9           | 1                    | 8                    | 9           | 0                    | 9                    | E | 8.0483374                | -1.3   |
| 9           | 2                    | 7                    | 9           | 1                    | 8                    | A | 19.4533553               | 0.6  |
| 9           | 2                    | 7                    | 9           | 1                    | 8                    | E | 19.4586916               | 6.2  |
| 9           | 2                    | 8                    | 9           | 1                    | 9                    | A | 21.6508731               | -6.6   |
| 9           | 2                    | 8                    | 9           | 1                    | 9                    | E | 21.6382726               | 8.6  |
| 9           | 3                    | 6                    | 9           | 2                    | 7                    | A | 34.0938677               | 6.9  |
| 9           | 3                    | 6                    | 9           | 2                    | 7                    | E | 34.1237390               | 2.0  |
| 9           | 3                    | 7                    | 9           | 2                    | 7                    | E | 34.0329110               | -5.7   |
| 9           | 3                    | 7                    | 9           | 2                    | 8                    | A | 34.1866384               | -0.9   |
| 9           | 3                    | 7                    | 9           | 2                    | 8                    | E | 34.1446660               | -3.5   |
| 8           | 3                    | 5                    | 8           | 2                    | 6                    | E | 34.1441011               | -2.2   |
| 8           | 3                    | 6                    | 8           | 2                    | 6                    | E | 34.0532699               | -3.3   |
| 8           | 3                    | 6                    | 8           | 2                    | 7                    | A | 34.1770063               | 4.4  |
| 8           | 3                    | 6                    | 8           | 2                    | 7                    | E | 34.1385722               | -2.4   |
| 8           | 4                    | 5                    | 9           | 3                    | 6                    | A | 34.9630766               | -3.0   |
| 9           | 0                    | 9                    | 8           | 1                    | 8                    | A | 6.8564779                | -1.0   |
| 9           | 0                    | 9                    | 8           | 1                    | 8                    | E | 6.8577666                | 8.1  |
| 9           | 1                    | 9                    | 8           | 0                    | 8                    | A | 18.5762211               | -4.0   |
| 9           | 1                    | 9                    | 8           | 0                    | 8                    | E | 18.5749365               | -1.8   |
| 9           | 1                    | 8                    | 9           | 0                    | 9                    | A | 8.0494922                | -2.0   |
| 9           | 1                    | 8                    | 9           | 0                    | 9                    | E | 8.0483374                | -1.3   |
| 9           | 2                    | 7                    | 9           | 1                    | 8                    | A | 19.4533553               | 0.6  |
| 9           | 2                    | 7                    | 9           | 1                    | 8                    | E | 19.4586916               | 6.2  |
| 9           | 2                    | 8                    | 9           | 1                    | 9                    | A | 21.6508731               | -6.6   |
| 9           | 2                    | 8                    | 9           | 1                    | 9                    | E | 21.6382726               | 8.6  |
| 9           | 3                    | 6                    | 9           | 2                    | 7                    | A | 34.0938677               | 6.9  |
| 9           | 3                    | 6                    | 9           | 2                    | 7                    | E | 34.1237390               | 2.0  |
| 9           | 3                    | 7                    | 9           | 2                    | 7                    | E | 34.0329110               | -5.7   |
| 9           | 3                    | 7                    | 9           | 2                    | 8                    | A | 34.1866384               | -0.9   |
| 9           | 3                    | 7                    | 9           | 2                    | 8                    | E | 34.1446660               | -3.5   |

**Figure S-1.** From left: the *a*-type A species transitions  $6_{16} \leftarrow 5_{15}$ ,  $6_{06} \leftarrow 5_{05}$ ,  $6_{25} \leftarrow 5_{24}$ ,  $6_{24} \leftarrow 5_{23}$ , and  $6_{15} \leftarrow 5_{14}$  of conformer I of methyl valerate. The frequencies (in GHz) are reproduced with the program *XIAM* using the rotational constants calculated at the MP2/6-311++G(d,p), and MP2/cc-pVDZ levels of theory and the experimentally deduced values.

