# Supporting Information for

# Rotational spectroscopy of the methyl glycidate–water complex: conformation and water and methyl rotor tunnelling motions

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**Completion of Ref. 26**. S5

**Table S1.** Calculated rotational constants and dipole moment components of the six most stable methyl glycidate-water complexes at the B3LYP-D3BJ/6-311++G(2d,p) level of theory.

| Parameter | MGly-1-W-I | MGly-2-W-II | MGly-2-W-III | MGly-1-W-IV | MGly-1-W-V | MGly-2-W-VI |
|---|---|---|---|---|---|---|
| $A$/MHz | 2887 | 2098 | 2021 | 3220 | 2542 | 4619 |
| $B$/MHz | 1265 | 1751 | 1538 | 1064 | 1332 | 912 |
| $C$/MHz | 945 | 1029 | 934 | 852 | 950 | 834 |
| $\|\mu_a\|$/D | 3.62 | 0.43 | 2.05 | 1.58 | 3.73 | 1.15 |
| $\|\mu_b\|$/D | 2.86 | 1.10 | 1.17 | 1.79 | 0.07 | 2.21 |
| $\|\mu_c\|$/D | 0.61 | 0.56 | 0.91 | 1.23 | 1.96 | 0.12 |

**Table S2.** A list of transitions included in the XIAM fit for the ortho MGly-1-W-I species.

| $J_{KaKc} - J'_{Ka'Kc'}$ | *SYM* | $\upsilon_{obs}$ / MHz | $J_{KaKc} - J'_{Ka'Kc'}$ | *SYM* | $\upsilon_{obs}$ / MHz |
|---|---|---|---|---|---|
| $2_{2\,0}$ - $1_{1\,1}$ | A | 9580.8983 (74) | $5_{1\,5}$ - $4_{0\,4}$ | A | 10538.3529 (-48) |
| | E | 9582.0384 (74) | | E | 10538.2978 (32) |
| $2_{2\,1}$ - $1_{1\,0}$ | A | 9195.0058 (9) | $5_{1\,5}$ - $4_{1\,4}$ | A | 9983.5219 (-65) |
| | E | 9193.2604 (-36) | | E | 9983.4981 (64) |
| $3_{1\,2}$ - $2_{1\,1}$ | A | 7067.9090 (48) | $5_{2\,3}$ - $4_{2\,2}$ | A | 11666.8709 (47) |
| | E | 7067.8073 (-6) | | E | 11666.6749 (6) |
| $3_{1\,3}$ - $2_{0\,2}$ | A | 7268.9367 (-48) | $5_{2\,4}$ - $4_{1\,3}$ | A | 14285.0551 (-157) |
| | E | 7268.8552 (79) | | E | 14284.7624 (-22) |
| $3_{2\,1}$ - $2_{1\,2}$ | A | 12311.1648 (-4) | $5_{2\,4}$ - $4_{2\,3}$ | A | 10886.6416 (-34) |
| | E | 12311.1003 (-76) | | E | 10866.6079 (2) |
| $3_{2\,1}$ - $2_{2\,0}$ | A | 6794.5479 (24) | $5_{2\,4}$ - $5_{1\,5}$ | A | 7621.0959 (55) |
| $3_{2\,2}$ - $2_{1\,1}$ | A | 11059.5289 (-18) | | E | 7620.6400 (15) |
| | E | 11058.9289 (-45) | $5_{3\,2}$ - $4_{3\,1}$ | A | 11224.8180 (22) |
| $3_{2\,2}$ - $2_{2\,1}$ | A | 6599.4121 (-29) | | E | 11221.6161 (-3) |
| | E | 6600.4609 (-37) | $5_{3\,3}$ - $4_{3\,2}$ | A | 11128.1442 (18) |
| $3_{3\,0}$ - $2_{2\,1}$ | A | 14904.5989 (-76) | | E | 11131.1234 (-3) |
| | E | 14916.1090 (30) | $5_{4\,2}$ - $4_{4\,1}$ | A | 11111.5167 (-112) |
| $3_{3\,1}$ - $2_{2\,0}$ | A | 14849.1781 (-95) | $6_{0\,6}$ - $5_{0\,5}$ | A | 12048.6598 (-100) |

| | | | | | |
|---|---|---|---|---|---|
| $4_{04}$ - $3_{03}$ | A | 8350.1352 (-23) | | E | 12048.6291 (66) |
| | E | 8350.0869 (24) | $6_{06}$ - $5_{15}$ | A | 11725.7326 (-44) |
| $4_{04}$ - $3_{13}$ | A | 7485.3794 (-29) | | E | 11725.7079 (46) |
| | E | 7485.3794 (16) | $6_{16}$ - $5_{05}$ | A | 12223.3582 (-74) |
| $4_{13}$ - $3_{12}$ | A | 9352.7863 (23) | | E | 12223.3196 (76) |
| | E | 9352.6658 (-4) | $6_{16}$ - $5_{15}$ | A | 11900.4270 (-58) |
| $4_{14}$ - $3_{03}$ | A | 8904.9618 (-50) | | E | 11900.4004 (76) |
| | E | 8904.8953 (55) | $6_{24}$ - $5_{23}$ | A | 14110.5923 (19) |
| $4_{14}$ - $3_{13}$ | A | 8040.2062 (-54) | | E | 14110.3951 (-18) |
| | E | 8040.1877 (70) | $6_{25}$ - $5_{24}$ | A | 12974.3932 (-21) |
| $4_{22}$ - $3_{21}$ | A | 9208.0956 (79) | | E | 12974.3176 (63) |
| | E | 9207.8020 (69) | $6_{33}$ - $5_{32}$ | A | 13604.8495 (9) |
| $4_{23}$ - $3_{12}$ | A | 12751.2081 (-16) | | E | 13603.9053 (-36) |
| | E | 12750.8231 (-26) | $6_{34}$ - $5_{33}$ | A | 13363.0982 (-33) |
| $4_{23}$ - $3_{22}$ | A | 8759.5845 (12) | | E | 13363.7699 (-8) |
| | E | 8759.7006 (30) | $6_{43}$ - $5_{42}$ | A | 13366.8581 (13) |
| $4_{32}$ - $3_{31}$ | A | 8887.6158 (206) | $7_{07}$ - $6_{06}$ | A | 13881.9959 (-82) |
| $5_{05}$ - $4_{04}$ | A | 10215.4248 (-56) | | E | 13881.9655 (74) |
| | E | 10215.3812 (57) | $7_{07}$ - $6_{16}$ | A | 13707.3023 (-60) |
| $5_{05}$ - $4_{14}$ | A | 9660.5962 (6) | | E | 13707.2748 (62) |
| | E | 9660.5711 (-14) | $7_{17}$ - $6_{06}$ | A | 13971.7282 (-72) |
| $5_{14}$ - $4_{13}$ | A | 11563.1758 (-1) | | E | 13971.6981 (105) |
| | E | 11563.0376 (-21) | $7_{17}$ - $6_{16}$ | A | 13797.0304 (-92) |
| | | | | E | 13797.0056 (75) |

[a] The residuals (obs-calc) are in parentheses in units of the last significant digits.

**Table S3.** A list of transitions included in the XIAM fit for the para MGly-1-W-I species.

| $J_{KaKc} - J'_{Ka'Kc'}$ | *SYM* | $\upsilon_{obs}$ / MHz | $J_{KaKc} - J'_{Ka'Kc'}$ | *SYM* | $\upsilon_{obs}$ / MHz |
|---|---|---|---|---|---|
| $2_{20}$ - $1_{11}$ | A | 9581.0644 (1661)[a] | $5_{23}$ - $4_{22}$ | A | 11666.8445 (-217) |
| | E | 9582.1945 (1590) | | E | 11666.6497 (-246) |
| $2_{21}$ - $1_{10}$ | A | 9195.1934 (1885) | $5_{24}$ - $4_{23}$ | A | 10886.7028 (578) |
| | E | 9193.4398 (1758) | | E | 10886.6741 (664) |

| | | | | | |
|---|---|---|---|---|---|
| $3_{2\,1}$ - $2_{1\,2}$ | A | 12311.2934 (1282) | $6_{0\,6}$ - $5_{0\,5}$ | A | 12048.8217 (1519) |
| | E | 12311.2291 (1212) | | E | 12048.7880 (1655) |
| $3_{2\,2}$ - $2_{1\,1}$ | A | 11059.7440 (2133) | $6_{0\,6}$ - $5_{1\,5}$ | A | 11725.8369 (999) |
| | E | 11059.1430 (2096) | | E | 11725.8161 (1128) |
| $4_{0\,4}$ - $3_{1\,3}$ | A | 7485.4034 (211) | $6_{1\,6}$ - $5_{0\,5}$ | A | 12223.5547 (1891) |
| | E | 7485.4034 (256) | | E | 12223.5176 (2056) |
| $4_{1\,3}$ - $3_{1\,2}$ | A | 9352.8119 (279) | $6_{1\,6}$ - $5_{1\,5}$ | A | 11900.5671 (1343) |
| | E | 9352.6929 (267) | | E | 11900.5417 (1489) |
| $4_{2\,2}$ - $3_{2\,1}$ | A | 9208.0765 (-112) | $6_{2\,4}$ - $5_{2\,3}$ | A | 14110.5728 (-178) |
| | E | 9207.7831 (-120) | | E | 14110.3766 (-203) |
| $4_{2\,3}$ - $3_{1\,2}$ | A | 12751.4580 (2483) | $6_{3\,4}$ - $5_{3\,3}$ | A | 13363.1367 (352) |
| | E | 12751.0668 (2437) | | E | 13363.8016 (309) |
| $5_{0\,5}$ - $4_{0\,4}$ | A | 10215.5475 (1227) | $7_{0\,7}$ - $6_{0\,6}$ | A | 13882.1848 (1807) |
| | E | 10215.5083 (1328) | | E | 13882.1519 (1938) |
| $5_{0\,5}$ - $4_{1\,4}$ | A | 9660.6565 (609) | $7_{0\,7}$ - $6_{1\,6}$ | A | 13707.4512 (1429) |
| | E | 9660.6354 (629) | | E | 13707.4244 (1558) |
| $5_{1\,4}$ - $4_{1\,3}$ | A | 11563.2172 (413) | $7_{1\,7}$ - $6_{0\,6}$ | A | 13971.9381 (2027) |
| | E | 11563.0825 (428) | | E | 13971.9057 (2181) |
| $5_{1\,5}$ - $4_{0\,4}$ | A | 10538.5343 (1766) | $7_{1\,7}$ - $6_{1\,6}$ | A | 13797.2037 (1641) |
| | E | 10538.4821 (1875) | | E | 13797.1766 (1785) |
| $5_{1\,5}$ - $4_{1\,4}$ | A | 9983.6355 (1071) | | | |
| | E | 9983.6090 (1173) | | | |

[a] The residuals (obs-calc) are in parentheses in units of the last significant digits.

**Table S4.** Calculated relative energies of the minima and transition states identified along the water tunnelling path in MGly-1-W-I.

| Level of theory | B3LYP-D3BJ/6-311++(2d,p) | | MP2/6-311++G(2d,p) | |
|---|---|---|---|---|
| | $\Delta E^{a}$ / kJmol$^{-1}$ | $\Delta E_{ZPE}{}^{a}$ / kJmol$^{-1}$ | $\Delta E^{a}$ / kJmol$^{-1}$ | $\Delta E_{ZPE}{}^{a}$ / kJmol$^{-1}$ |
| **I** | 0.0 | 0.0 | 0.0 | 0.0 |
| **T1** | 3.9 | 2.0 | 3.4 | 1.9 |
| **II** | 3.2 | 2.3 | 2.8 | 2.3 |
| **T2** | 3.5 | 1.7 | 2.9 | 1.7 |
| **I’** | 0.0 | 0.0 | 0.0 | 0.0 |

[a] Relative energy to **I** (or **I’**) without or with ZPE correction.

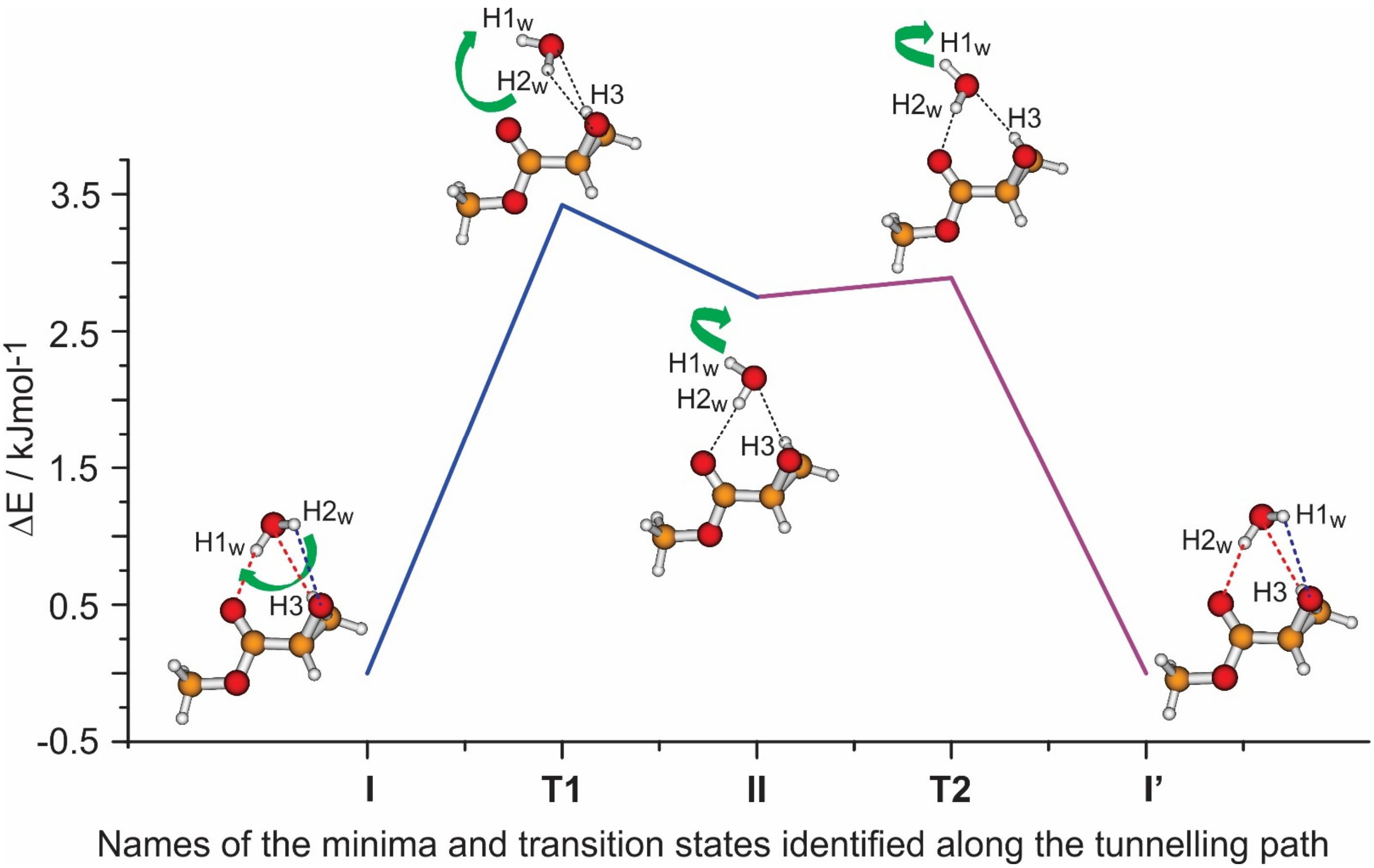


**Figure S1.** The relative energies of the minima and transition states identified along the water tunnelling path in MGly1-W-I, the most stable methyl glycidate-water complex, at the B3LYP-D3BJ/6-311++G(2d,p) level of theory, without zero-point energy correction. After zero-point energy correction, **II** becomes slightly higher in energy than **T1** and **T2** (see Table S4). The water tunnelling path consists of two different water motions. See the main text for a detailed description.

**Completion of Ref. 26.**


Gaussian 09 (Revision D.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.