

# A Butterfly Motion of Formic Acid and Cyclobutanone in the 1:1 Hydrogen Bonded Molecular Cluster†

Luca Evangelisti,<sup>a</sup> Lorenzo Spada,<sup>a</sup> Weixing Li,<sup>a</sup> Susana Blanco,<sup>b</sup> Juan Carlos López,<sup>b</sup>

Alberto Lesarri,<sup>\*b</sup> Jens-Uwe Grabow,<sup>c</sup> Walther Caminati<sup>\*a</sup>

## ***Electronic Supporting Information***

---

<sup>a</sup>Dipartimento di Chimica “G. Ciamician” dell’Università, Via Selmi 2, I-40126 Bologna, Italy. E-mail: [walther.caminati@unibo.it](mailto:walther.caminati@unibo.it)

<sup>b</sup>Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain. E-mail: [lesarri@qf.uva.es](mailto:lesarri@qf.uva.es)

<sup>c</sup>Institut für Physikalische Chemie und Elektrochemie, Lehrgebiet A, Gottfried-Wilhelm-Leibniz-Universität, Callinstrasse 3A, D-30167 Hannover, Germany

**Table S1.** Measured line frequencies ( $\nu/\text{MHz}$ ) and observed-calculated values ( $\Delta\nu/\text{kHz}$ ) of HCOOH-CBU.

| N  | $J'$ | $K_a'$ | $K_c'$ | $\nu'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu''$ | $\nu/\text{MHz}$ | $\Delta\nu/\text{kHz}$ |
|----|------|--------|--------|--------|-------|---------|---------|---------|------------------|------------------------|
| 1  | 4    | 0      | 4      | 1      | 3     | 0       | 3       | 1       | 7279.7897        | -5.3                   |
| 2  | 4    | 0      | 4      | 0      | 3     | 0       | 3       | 0       | 7278.5599        | 3.4                    |
| 3  | 4    | 1      | 4      | 1      | 3     | 1       | 3       | 1       | 7017.0642        | 1.8                    |
| 4  | 4    | 1      | 4      | 0      | 3     | 1       | 3       | 0       | 7026.9827        | 8.0                    |
| 5  | 4    | 1      | 3      | 1      | 3     | 1       | 2       | 1       | 7608.7788        | -1.4                   |
| 6  | 4    | 1      | 3      | 0      | 3     | 1       | 2       | 0       | 7619.3977        | -4.4                   |
| 7  | 4    | 2      | 2      | 1      | 3     | 2       | 1       | 1       | 7373.0216        | -6.4                   |
| 8  | 4    | 2      | 2      | 0      | 3     | 2       | 1       | 0       | 7371.8964        | 0.8                    |
| 9  | 4    | 2      | 3      | 1      | 3     | 2       | 2       | 1       | 7324.9138        | -5.5                   |
| 10 | 4    | 2      | 3      | 0      | 3     | 2       | 2       | 0       | 7323.7302        | 4.4                    |
| 11 | 5    | 0      | 5      | 1      | 4     | 0       | 4       | 1       | 9064.1524        | -2.4                   |
| 12 | 5    | 0      | 5      | 0      | 4     | 0       | 4       | 0       | 9062.5619        | 4.9                    |
| 13 | 5    | 1      | 5      | 1      | 4     | 1       | 4       | 1       | 8780.1124        | -7.4                   |
| 14 | 5    | 1      | 5      | 0      | 4     | 1       | 4       | 0       | 8775.0086        | 6.1                    |
| 15 | 5    | 1      | 4      | 1      | 4     | 1       | 3       | 1       | 9501.0683        | -2.7                   |
| 16 | 5    | 1      | 4      | 0      | 4     | 1       | 3       | 0       | 9496.8392        | 5.4                    |
| 17 | 5    | 2      | 4      | 1      | 4     | 2       | 3       | 1       | 9150.1847        | -4.8                   |
| 18 | 5    | 2      | 4      | 0      | 4     | 2       | 3       | 0       | 9148.5579        | 3.3                    |
| 19 | 5    | 2      | 3      | 1      | 4     | 2       | 2       | 1       | 9245.4086        | -4.0                   |
| 20 | 5    | 2      | 3      | 0      | 4     | 2       | 2       | 0       | 9243.9018        | 3.3                    |
| 21 | 6    | 0      | 6      | 1      | 5     | 0       | 5       | 1       | 10826.8385       | -0.4                   |
| 22 | 6    | 0      | 6      | 0      | 5     | 0       | 5       | 0       | 10824.8584       | 3.1                    |
| 23 | 6    | 1      | 6      | 1      | 5     | 1       | 5       | 1       | 10520.7594       | -5.4                   |
| 24 | 6    | 1      | 6      | 0      | 5     | 1       | 5       | 0       | 10517.8301       | 3.9                    |
| 25 | 6    | 1      | 5      | 1      | 5     | 1       | 4       | 1       | 11386.1088       | -0.6                   |
| 26 | 6    | 1      | 5      | 0      | 5     | 1       | 4       | 0       | 11384.2211       | 2.0                    |
| 27 | 6    | 2      | 5      | 1      | 5     | 2       | 4       | 1       | 10971.7377       | -6.1                   |
| 28 | 6    | 2      | 5      | 0      | 5     | 2       | 4       | 0       | 10969.2396       | 6.3                    |
| 29 | 6    | 2      | 4      | 0      | 5     | 2       | 3       | 0       | 11132.9333       | 0.2                    |
| 30 | 6    | 2      | 4      | 1      | 5     | 2       | 3       | 1       | 11135.2304       | -5.8                   |
| 31 | 7    | 0      | 7      | 1      | 6     | 0       | 6       | 1       | 12566.5864       | 2.5                    |
| 32 | 7    | 0      | 7      | 0      | 6     | 0       | 6       | 0       | 12564.1892       | 1.0                    |
| 33 | 7    | 1      | 7      | 1      | 6     | 1       | 6       | 1       | 12257.8812       | 1.1                    |
| 34 | 7    | 1      | 7      | 0      | 6     | 1       | 6       | 0       | 12254.9125       | 2.7                    |
| 35 | 7    | 1      | 6      | 1      | 6     | 1       | 5       | 1       | 13261.8654       | -1.3                   |
| 36 | 7    | 1      | 6      | 0      | 6     | 1       | 5       | 0       | 13260.1086       | -1.5                   |
| 37 | 7    | 2      | 6      | 1      | 6     | 2       | 5       | 1       | 12789.9384       | -2.7                   |
| 38 | 7    | 2      | 6      | 0      | 6     | 2       | 5       | 0       | 12784.8966       | 4.4                    |
| 39 | 7    | 2      | 5      | 0      | 6     | 2       | 4       | 0       | 13038.2176       | 2.0                    |
| 40 | 7    | 2      | 5      | 1      | 6     | 2       | 4       | 1       | 13042.9435       | 0.9                    |
| 41 | 8    | 1      | 8      | 1      | 7     | 1       | 7       | 1       | 13989.2216       | 3.7                    |
| 42 | 8    | 1      | 8      | 0      | 7     | 1       | 7       | 0       | 13985.9480       | 0.3                    |

|    |    |   |    |   |   |   |   |   |            |       |
|----|----|---|----|---|---|---|---|---|------------|-------|
| 43 | 8  | 1 | 7  | 1 | 7 | 1 | 6 | 1 | 15126.0221 | 2.7   |
| 44 | 8  | 1 | 7  | 0 | 7 | 1 | 6 | 0 | 15124.1189 | -4.1  |
| 45 | 8  | 2 | 6  | 1 | 7 | 2 | 5 | 1 | 14966.6261 | 0.8   |
| 46 | 8  | 2 | 6  | 0 | 7 | 2 | 5 | 0 | 14944.1480 | -4.5  |
| 47 | 8  | 2 | 7  | 0 | 7 | 2 | 6 | 0 | 14594.7261 | 2.2   |
| 48 | 8  | 2 | 7  | 1 | 7 | 2 | 6 | 1 | 14617.6611 | 2.3   |
| 49 | 9  | 0 | 9  | 1 | 8 | 0 | 8 | 1 | 15983.5382 | 5.0   |
| 50 | 9  | 0 | 9  | 0 | 8 | 0 | 8 | 0 | 15980.2385 | -6.1  |
| 51 | 9  | 1 | 9  | 1 | 8 | 1 | 8 | 1 | 15714.5178 | 4.8   |
| 52 | 9  | 1 | 9  | 0 | 8 | 1 | 8 | 0 | 15710.8593 | -7.5  |
| 53 | 9  | 1 | 8  | 1 | 8 | 1 | 7 | 1 | 16975.9494 | 4.8   |
| 54 | 9  | 1 | 8  | 0 | 8 | 1 | 7 | 0 | 16973.8181 | -5.7  |
| 55 | 9  | 2 | 8  | 1 | 8 | 2 | 7 | 1 | 16350.4797 | 0.7   |
| 56 | 9  | 2 | 8  | 0 | 8 | 2 | 7 | 0 | 16398.0087 | -2.4  |
| 57 | 9  | 2 | 7  | 0 | 8 | 2 | 6 | 0 | 16950.2037 | -1.5  |
| 58 | 9  | 2 | 7  | 1 | 8 | 2 | 6 | 1 | 16902.0546 | 4.9   |
| 59 | 10 | 0 | 10 | 1 | 9 | 0 | 9 | 1 | 17668.7085 | 12.0  |
| 60 | 10 | 0 | 10 | 0 | 9 | 0 | 9 | 0 | 17664.9263 | -10.7 |
| 61 | 10 | 1 | 10 | 1 | 9 | 1 | 9 | 1 | 17433.8730 | 9.5   |
| 62 | 10 | 1 | 10 | 0 | 9 | 1 | 9 | 0 | 17429.7979 | -12.0 |
| 63 | 3  | 1 | 3  | 1 | 2 | 0 | 2 | 1 | 8302.5384  | -10.6 |
| 64 | 3  | 1 | 3  | 0 | 2 | 0 | 2 | 0 | 8297.6474  | 3.7   |
| 65 | 4  | 1 | 4  | 1 | 3 | 0 | 3 | 1 | 9842.7974  | -3.0  |
| 66 | 4  | 1 | 4  | 0 | 3 | 0 | 3 | 0 | 9848.7145  | 3.5   |
| 67 | 5  | 1 | 5  | 1 | 4 | 0 | 4 | 1 | 11343.1152 | -9.9  |
| 68 | 5  | 1 | 5  | 0 | 4 | 0 | 4 | 0 | 11345.1613 | 4.3   |
| 69 | 6  | 1 | 6  | 1 | 5 | 0 | 5 | 1 | 12799.7275 | -7.6  |
| 70 | 6  | 1 | 6  | 0 | 5 | 0 | 5 | 0 | 12800.4374 | 11.1  |
| 71 | 6  | 0 | 6  | 1 | 5 | 1 | 5 | 1 | 8547.8685  | -0.1  |
| 72 | 6  | 0 | 6  | 0 | 5 | 1 | 5 | 0 | 8542.2551  | -0.2  |
| 73 | 7  | 0 | 7  | 1 | 6 | 1 | 6 | 1 | 10593.6900 | 2.3   |
| 74 | 7  | 0 | 7  | 0 | 6 | 1 | 6 | 0 | 10588.6119 | -5.4  |
| 75 | 3  | 1 | 2  | 1 | 2 | 0 | 2 | 0 | 10292.3525 | -4.3  |
| 76 | 3  | 1 | 2  | 0 | 2 | 0 | 2 | 1 | 8041.2570  | -0.7  |
| 77 | 4  | 1 | 3  | 1 | 3 | 0 | 3 | 0 | 12425.2303 | 0.8   |
| 78 | 4  | 1 | 3  | 0 | 3 | 0 | 3 | 1 | 10183.8584 | 9.6   |
| 79 | 2  | 2 | 1  | 0 | 1 | 1 | 0 | 0 | 13299.2176 | 3.9   |
| 80 | 2  | 2 | 1  | 1 | 1 | 1 | 0 | 1 | 13297.3366 | 3.2   |
| 81 | 2  | 2 | 0  | 0 | 1 | 1 | 1 | 0 | 13449.1731 | 1.4   |
| 82 | 2  | 2 | 0  | 1 | 1 | 1 | 1 | 1 | 13447.1083 | 4.4   |
| 83 | 2  | 2 | 1  | 0 | 1 | 1 | 1 | 1 | 12321.9640 | -5.7  |
| 84 | 2  | 2 | 0  | 0 | 1 | 1 | 0 | 1 | 12181.8855 | -7.2  |

**Table S2.** Measured line frequencies ( $\nu$ /MHz) and observed-calculated values ( $\Delta\nu$ /kHz) of DCOOH-CBU.

| N  | $J'$ | $K_a'$ | $K_c'$ | $\nu'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu''$ | $\nu$ /MHz | $\Delta\nu$ /kHz |
|----|------|--------|--------|--------|-------|---------|---------|---------|------------|------------------|
| 1  | 4    | 0      | 4      | 1      | 3     | 0       | 3       | 1       | 7096.5666  | -3.0             |
| 2  | 4    | 0      | 4      | 0      | 3     | 0       | 3       | 0       | 7095.4035  | 6.0              |
| 3  | 4    | 1      | 4      | 1      | 3     | 1       | 3       | 1       | 6844.4701  | -1.4             |
| 4  | 4    | 1      | 4      | 0      | 3     | 1       | 3       | 0       | 6853.8341  | 2.8              |
| 5  | 4    | 1      | 3      | 1      | 3     | 1       | 2       | 1       | 7408.2407  | 4.1              |
| 6  | 4    | 1      | 3      | 0      | 3     | 1       | 2       | 0       | 7418.2460  | -3.4             |
| 7  | 5    | 0      | 5      | 1      | 4     | 0       | 4       | 1       | 8838.3997  | -2.2             |
| 8  | 5    | 0      | 5      | 0      | 4     | 0       | 4       | 0       | 8836.8973  | 4.9              |
| 9  | 5    | 1      | 5      | 1      | 4     | 1       | 4       | 1       | 8564.4200  | -7.1             |
| 10 | 5    | 1      | 5      | 0      | 4     | 1       | 4       | 0       | 8559.3704  | 5.2              |
| 11 | 5    | 1      | 4      | 1      | 4     | 1       | 3       | 1       | 9251.3639  | -1.1             |
| 12 | 5    | 1      | 4      | 0      | 4     | 1       | 3       | 0       | 9247.1122  | -0.4             |
| 13 | 5    | 2      | 4      | 1      | 4     | 2       | 3       | 1       | 8916.3803  | -4.9             |
| 14 | 5    | 2      | 4      | 0      | 4     | 2       | 3       | 0       | 8914.8548  | 3.7              |
| 15 | 5    | 2      | 3      | 1      | 4     | 2       | 2       | 1       | 9002.7076  | -2.9             |
| 16 | 5    | 2      | 3      | 0      | 4     | 2       | 2       | 0       | 9001.2854  | 2.5              |
| 17 | 6    | 0      | 6      | 1      | 5     | 0       | 5       | 1       | 10560.3784 | -4.1             |
| 18 | 6    | 0      | 6      | 0      | 5     | 0       | 5       | 0       | 10558.5161 | 4.4              |
| 19 | 6    | 1      | 6      | 1      | 5     | 1       | 5       | 1       | 10262.9303 | -6.2             |
| 20 | 6    | 1      | 6      | 0      | 5     | 1       | 5       | 0       | 10260.1505 | 6.1              |
| 21 | 6    | 1      | 5      | 1      | 5     | 1       | 4       | 1       | 11087.9781 | 1.7              |
| 22 | 6    | 1      | 5      | 0      | 5     | 1       | 4       | 0       | 11086.1464 | -2.1             |
| 23 | 7    | 0      | 7      | 1      | 6     | 0       | 6       | 1       | 12261.1035 | 0.2              |
| 24 | 7    | 0      | 7      | 0      | 6     | 0       | 6       | 0       | 12258.8492 | 1.6              |
| 25 | 7    | 1      | 7      | 1      | 6     | 1       | 6       | 1       | 11958.4514 | -7.4             |
| 26 | 7    | 1      | 7      | 0      | 6     | 1       | 6       | 0       | 11955.6587 | 3.9              |
| 27 | 7    | 1      | 6      | 1      | 6     | 1       | 5       | 1       | 12916.2732 | 3.0              |
| 28 | 7    | 1      | 6      | 0      | 6     | 1       | 5       | 0       | 12914.5808 | -1.8             |
| 29 | 9    | 0      | 9      | 1      | 8     | 0       | 8       | 1       | 15603.0404 | 7.2              |
| 30 | 9    | 0      | 9      | 0      | 8     | 0       | 8       | 0       | 15599.9425 | -2.3             |
| 31 | 9    | 1      | 9      | 1      | 8     | 1       | 8       | 1       | 15333.2655 | 7.6              |
| 32 | 9    | 1      | 9      | 0      | 8     | 1       | 8       | 0       | 15329.8211 | -4.8             |
| 33 | 9    | 1      | 8      | 1      | 8     | 1       | 7       | 1       | 16539.4154 | 7.7              |
| 34 | 9    | 1      | 8      | 0      | 8     | 1       | 7       | 0       | 16537.3740 | -7.8             |
| 35 | 10   | 0      | 10     | 1      | 9     | 0       | 9       | 1       | 17250.8947 | 2.6              |
| 36 | 10   | 0      | 10     | 0      | 9     | 0       | 9       | 0       | 17247.3539 | -10.1            |
| 37 | 10   | 1      | 10     | 1      | 9     | 1       | 9       | 1       | 17012.2929 | 11.0             |
| 38 | 10   | 1      | 10     | 0      | 9     | 1       | 9       | 0       | 17008.4604 | -8.4             |
| 39 | 3    | 1      | 3      | 1      | 2     | 0       | 2       | 1       | 8192.4925  | 0.9              |
| 40 | 3    | 1      | 3      | 0      | 2     | 0       | 2       | 0       | 8188.1869  | -4.3             |
| 41 | 4    | 1      | 4      | 1      | 3     | 0       | 3       | 1       | 9699.1692  | 3.3              |
| 42 | 4    | 1      | 4      | 0      | 3     | 0       | 3       | 0       | 9705.0794  | -2.3             |

|    |   |   |   |   |   |   |   |   |            |       |
|----|---|---|---|---|---|---|---|---|------------|-------|
| 43 | 5 | 1 | 5 | 1 | 4 | 0 | 4 | 1 | 11167.0127 | -10.6 |
| 44 | 5 | 1 | 5 | 0 | 4 | 0 | 4 | 0 | 11169.0557 | 6.3   |
| 45 | 6 | 1 | 6 | 1 | 5 | 0 | 5 | 1 | 12591.5526 | -5.3  |
| 46 | 6 | 1 | 6 | 0 | 5 | 0 | 5 | 0 | 12592.3098 | 8.4   |
| 47 | 6 | 0 | 6 | 1 | 5 | 1 | 5 | 1 | 8231.7545  | -6.6  |
| 48 | 6 | 0 | 6 | 0 | 5 | 1 | 5 | 0 | 8226.3572  | 2.5   |
| 49 | 7 | 0 | 7 | 1 | 6 | 1 | 6 | 1 | 10229.9241 | -3.8  |
| 50 | 7 | 0 | 7 | 0 | 6 | 1 | 6 | 0 | 10225.0630 | 5.0   |
| 51 | 3 | 1 | 2 | 1 | 2 | 0 | 2 | 0 | 10103.5147 | 4.3   |
| 52 | 3 | 1 | 2 | 0 | 2 | 0 | 2 | 1 | 7929.4514  | -4.3  |
| 53 | 4 | 1 | 3 | 1 | 3 | 0 | 3 | 0 | 12174.8025 | -3.8  |
| 54 | 4 | 1 | 3 | 0 | 3 | 0 | 3 | 1 | 10009.9125 | 4.7   |

**Table S3.** Measured line frequencies ( $\nu$ /MHz) and observed-calculated values ( $\Delta\nu$ /kHz) of HCOOD-CBU.

| N  | $J'$ | $K_a'$ | $K_c'$ | $\nu'$ | $J''$ | $K_a''$ | $K_c''$ | $\nu''$ | $\nu$ /MHz | $\Delta\nu$ /kHz |
|----|------|--------|--------|--------|-------|---------|---------|---------|------------|------------------|
| 1  | 4    | 0      | 4      | 1      | 3     | 0       | 3       | 1       | 7240.6720  | -6.0             |
| 2  | 4    | 0      | 4      | 0      | 3     | 0       | 3       | 0       | 7239.3814  | 0.7              |
| 3  | 4    | 1      | 4      | 1      | 3     | 1       | 3       | 1       | 6977.1175  | 5.2              |
| 4  | 4    | 1      | 4      | 0      | 3     | 1       | 3       | 0       | 6988.0793  | 6.7              |
| 5  | 4    | 1      | 3      | 1      | 3     | 1       | 2       | 1       | 7570.0873  | -1.7             |
| 6  | 4    | 1      | 3      | 0      | 3     | 1       | 2       | 0       | 7581.7734  | -6.6             |
| 7  | 4    | 2      | 2      | 1      | 3     | 2       | 1       | 1       | 7334.7673  | 3.8              |
| 8  | 4    | 2      | 2      | 0      | 3     | 2       | 1       | 0       | 7333.5878  | 10.4             |
| 9  | 4    | 2      | 3      | 1      | 3     | 2       | 2       | 1       | 7286.2186  | 1.3              |
| 10 | 4    | 2      | 3      | 0      | 3     | 2       | 2       | 0       | 7284.9803  | 10.4             |
| 11 | 5    | 0      | 5      | 1      | 4     | 0       | 4       | 1       | 9014.9450  | -5.2             |
| 12 | 5    | 0      | 5      | 0      | 4     | 0       | 4       | 0       | 9013.2831  | 4.5              |
| 13 | 5    | 1      | 5      | 1      | 4     | 1       | 4       | 1       | 8732.8518  | -6.6             |
| 14 | 5    | 1      | 5      | 0      | 4     | 1       | 4       | 0       | 8726.3019  | 3.0              |
| 15 | 5    | 1      | 4      | 1      | 4     | 1       | 3       | 1       | 9452.6176  | 2.7              |
| 16 | 5    | 1      | 4      | 0      | 4     | 1       | 3       | 0       | 9446.9658  | 4.1              |
| 17 | 5    | 2      | 4      | 1      | 4     | 2       | 3       | 1       | 9101.7470  | -9.4             |
| 18 | 5    | 2      | 4      | 0      | 4     | 2       | 3       | 0       | 9100.0595  | -0.3             |
| 19 | 5    | 2      | 3      | 1      | 4     | 2       | 2       | 1       | 9197.8209  | -9.6             |
| 20 | 5    | 2      | 3      | 0      | 4     | 2       | 2       | 0       | 9196.2569  | 1.5              |
| 21 | 6    | 0      | 6      | 1      | 5     | 0       | 5       | 1       | 10767.3934 | -1.0             |
| 22 | 6    | 0      | 6      | 0      | 5     | 0       | 5       | 0       | 10765.3254 | 3.6              |
| 23 | 6    | 1      | 6      | 1      | 5     | 1       | 5       | 1       | 10462.4631 | -4.3             |
| 24 | 6    | 1      | 6      | 0      | 5     | 1       | 5       | 0       | 10459.2894 | 7.1              |
| 25 | 6    | 1      | 5      | 1      | 5     | 1       | 4       | 1       | 11327.8150 | 1.4              |
| 26 | 6    | 1      | 5      | 0      | 5     | 1       | 4       | 0       | 11325.7118 | 3.3              |
| 27 | 6    | 2      | 5      | 1      | 5     | 2       | 4       | 1       | 10913.5231 | -5.5             |
| 28 | 6    | 2      | 5      | 0      | 5     | 2       | 4       | 0       | 10910.9671 | 1.4              |
| 29 | 6    | 2      | 4      | 0      | 5     | 2       | 3       | 0       | 11076.0979 | 2.5              |
| 30 | 6    | 2      | 4      | 1      | 5     | 2       | 3       | 1       | 11078.4445 | -5.3             |
| 31 | 7    | 0      | 7      | 1      | 6     | 0       | 6       | 1       | 12496.7878 | -0.9             |
| 32 | 7    | 0      | 7      | 0      | 6     | 0       | 6       | 0       | 12494.2924 | 4.1              |
| 33 | 7    | 1      | 7      | 1      | 6     | 1       | 6       | 1       | 12189.6260 | 2.0              |
| 34 | 7    | 1      | 7      | 0      | 6     | 1       | 6       | 0       | 12186.4884 | 0.0              |
| 35 | 7    | 1      | 6      | 1      | 6     | 1       | 5       | 1       | 13193.6314 | 1.0              |
| 36 | 7    | 1      | 6      | 0      | 6     | 1       | 5       | 0       | 13191.7407 | -4.8             |
| 37 | 7    | 2      | 6      | 1      | 6     | 2       | 5       | 1       | 12721.7689 | -0.7             |
| 38 | 7    | 2      | 6      | 0      | 6     | 2       | 5       | 0       | 12716.8082 | -0.4             |
| 39 | 7    | 2      | 5      | 0      | 6     | 2       | 4       | 0       | 12972.3787 | -2.1             |
| 40 | 7    | 2      | 5      | 1      | 6     | 2       | 4       | 1       | 12977.0177 | -0.1             |
| 41 | 8    | 1      | 8      | 1      | 7     | 1       | 7       | 1       | 13911.0488 | 4.5              |
| 42 | 8    | 1      | 8      | 0      | 7     | 1       | 7       | 0       | 13907.6116 | -4.7             |

|    |   |   |   |   |   |   |   |   |            |      |
|----|---|---|---|---|---|---|---|---|------------|------|
| 43 | 8 | 1 | 7 | 1 | 7 | 1 | 6 | 1 | 15047.7112 | 0.4  |
| 44 | 8 | 1 | 7 | 0 | 7 | 1 | 6 | 0 | 15045.6991 | -0.1 |
| 45 | 8 | 2 | 6 | 1 | 7 | 2 | 5 | 1 | 14891.5405 | -2.9 |
| 46 | 8 | 2 | 6 | 0 | 7 | 2 | 5 | 0 | 14872.5905 | -4.3 |
| 47 | 8 | 2 | 7 | 0 | 7 | 2 | 6 | 0 | 14516.7717 | 0.4  |
| 48 | 8 | 2 | 7 | 1 | 7 | 2 | 6 | 1 | 14536.1917 | 5.9  |
| 49 | 9 | 0 | 9 | 1 | 8 | 0 | 8 | 1 | 15893.0466 | 7.6  |
| 50 | 9 | 0 | 9 | 0 | 8 | 0 | 8 | 0 | 15889.6060 | -6.2 |
| 51 | 9 | 1 | 9 | 1 | 8 | 1 | 8 | 1 | 15626.4200 | 7.4  |
| 52 | 9 | 1 | 9 | 0 | 8 | 1 | 8 | 0 | 15622.5911 | -9.4 |
| 53 | 9 | 1 | 8 | 1 | 8 | 1 | 7 | 1 | 16887.4043 | 6.0  |
| 54 | 9 | 1 | 8 | 0 | 8 | 1 | 7 | 0 | 16885.1519 | -7.5 |
| 55 | 9 | 2 | 8 | 1 | 8 | 2 | 7 | 1 | 16261.7211 | 2.6  |
| 56 | 9 | 2 | 8 | 0 | 8 | 2 | 7 | 0 | 16310.1263 | -3.2 |
| 57 | 9 | 2 | 7 | 0 | 8 | 2 | 6 | 0 | 16866.7305 | 2.3  |
| 58 | 9 | 2 | 7 | 1 | 8 | 2 | 6 | 1 | 16817.6915 | 3.8  |
| 59 | 4 | 1 | 4 | 1 | 3 | 0 | 3 | 1 | 9774.4162  | -4.9 |
| 60 | 4 | 1 | 4 | 0 | 3 | 0 | 3 | 0 | 9782.0535  | 0.5  |
| 61 | 5 | 1 | 5 | 1 | 4 | 0 | 4 | 1 | 11266.5972 | -4.3 |
| 62 | 5 | 1 | 5 | 0 | 4 | 0 | 4 | 0 | 11268.9754 | 4.2  |
| 63 | 6 | 1 | 6 | 1 | 5 | 0 | 5 | 1 | 12714.1154 | -3.2 |
| 64 | 6 | 1 | 6 | 0 | 5 | 0 | 5 | 0 | 12714.9757 | 0.8  |
| 65 | 6 | 0 | 6 | 1 | 5 | 1 | 5 | 1 | 8515.7388  | -4.3 |
| 66 | 6 | 0 | 6 | 0 | 5 | 1 | 5 | 0 | 8509.6303  | 1.0  |
| 67 | 7 | 0 | 7 | 1 | 6 | 1 | 6 | 1 | 10550.0638 | -0.6 |
| 68 | 7 | 0 | 7 | 0 | 6 | 1 | 6 | 0 | 10544.6347 | -0.6 |
| 69 | 4 | 1 | 3 | 1 | 3 | 0 | 3 | 0 | 12416.6010 | 1.9  |
| 70 | 4 | 1 | 3 | 0 | 3 | 0 | 3 | 1 | 10061.7668 | 0.8  |
| 71 | 2 | 2 | 1 | 0 | 1 | 1 | 0 | 0 | 13196.3426 | 1.6  |
| 72 | 2 | 2 | 1 | 1 | 1 | 1 | 0 | 1 | 13194.4037 | 1.9  |
| 73 | 2 | 2 | 0 | 0 | 1 | 1 | 1 | 0 | 13346.3847 | -4.1 |
| 74 | 2 | 2 | 0 | 1 | 1 | 1 | 1 | 1 | 13344.2574 | 0.7  |

**Table S4.** B3LYP-D3/6-311++G(d,p) cartesian coordinates of the HCOOH-CBU cluster in the principal axes of inertia.

| ATOM | $a / \text{\AA}$ | $b / \text{\AA}$ | $c / \text{\AA}$ |
|------|------------------|------------------|------------------|
| C    | 2.7146           | 0.3856           | -0.0477          |
| O    | 2.4242           | -0.8644          | 0.2959           |
| O    | 1.9302           | 1.2197           | -0.4327          |
| H    | 1.4554           | -1.0366          | 0.1813           |
| H    | 3.7927           | 0.5710           | 0.0684           |
| O    | -0.2479          | -1.3883          | -0.0700          |
| C    | -1.1143          | -0.5510          | 0.0203           |
| C    | -1.1539          | 0.8774           | 0.5468           |
| C    | -2.6426          | 0.9556           | 0.0830           |
| C    | -2.5820          | -0.5312          | -0.3943          |
| H    | -2.7418          | -0.7167          | -1.4594          |
| H    | -3.1933          | -1.2379          | 0.1738           |
| H    | -2.8133          | 1.6685           | -0.7230          |
| H    | -3.3598          | 1.1446           | 0.8810           |
| H    | -0.4315          | 1.5322           | 0.0557           |
| H    | -0.9881          | 0.9368           | 1.6265           |

**Table S5.** B3LYP-D3/6-311++G(d,p) cartesian coordinates of the transition state of the cluster HCOOH-CBU in the principal axes of inertia.

| ATOM | $a / \text{\AA}$ | $b / \text{\AA}$ | $c / \text{\AA}$ |
|------|------------------|------------------|------------------|
| C    | -2.7529          | 0.3591           | 0.0000           |
| O    | -2.4575          | -0.9360          | 0.0000           |
| O    | -1.9581          | 1.2686           | 0.0000           |
| H    | -1.4748          | -1.0601          | 0.0000           |
| H    | -3.8438          | 0.5014           | 0.0000           |
| O    | 0.2567           | -1.3701          | 0.0000           |
| C    | 1.1238           | -0.5285          | 0.0000           |
| C    | 1.1311           | 0.9954           | 0.0000           |
| C    | 2.6911           | 0.9411           | 0.0000           |
| C    | 2.6463           | -0.6206          | 0.0000           |
| H    | 3.1543           | 1.3733           | 0.8865           |
| H    | 3.1540           | 1.3732           | -0.8866          |
| H    | 3.0496           | -1.1185          | 0.8859           |
| H    | 3.0493           | -1.1179          | -0.8863          |
| H    | 0.6467           | 1.4318           | 0.8758           |
| H    | 0.6480           | 1.4302           | -0.8773          |