**Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.**

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# Tetrel Bond and Conformational Equilibria in the Formamide – $CO_2$ Complex: A Rotational Study

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**Table S1.** The calculated spectroscopic parameters of the three isomers of the FM-$CO_2$ complex at different levels of theory.

| | | | *A/B/C*MHz | $\Delta E_0$/cm$^{-1}$ | $\Delta G$/cm$^{-1}$ |
|---|---|---|---|---|---|
| B3lyp-D3BJ | 6-311++G(d,p) | **I** | 6975.1/1952.8/1525.6 | 0 | 0 |
| | | **II** | 10023.8/1481.9/1291.0 | 271 | 399 |
| | | **III** | 19862.0/778.1/753.1 | 819 | 931 |
| | aug-cc-pVTZ | **I** | 6985.0/1959.1/1527.1 | 0 | 0 |
| | | **II** | 10065.2/1485.2/1292.5 | 244 | 381 |
| | | **III** | 22774.0/756.1/731.9 | 776 | 896 |
| MP2 | 6-311++G(d,p) | **I** | 6848.7/1888.0/1482.8 | 0 | 0 |
| | | **II** | 9790.2/1448.6/1262.5 | 217 | 349 |
| | | **III** | 21868.5/753.0/734.6 | 638 | 734 |
| | aug-cc-pVTZ | **I** | 6923.5/1979.9/1534.6 | 0 | 0 |
| | | **II** | 9783.4/1507.8/1306.5 | 250 | 399 |
| | | **III** | 20077.6/729.3/712.1 | 711 | 883 |
| M06-2X | 6-311++G(d,p) | **I** | 7196.8/2033.8/1585.7 | 0 | 0 |
| | | **II** | 10212.3/1557.8/1351.6 | 217 | 357 |
| | | **III** | 14830.8/900.0/849.8 | 574 | 614 |
| | aug-cc-pVTZ | **I** | 7113.4/2035.9/1582.9 | 0 | 0 |
| | | **II** | 10130.2/1561.2/1352.7 | 216 | 390 |
| | | **III** | 14936.9/892.7/833.4 | 841 | 822 |
| Wb97xd | 6-311++G(d,p) | **I** | 7034.4/1969.6/1531.3 | 0 | 0 |
| | | **II** | 10097.4/1490.9/1293.9 | 217 | 357 |
| | | **III** | 15480.9/827.3/790.3 | 574 | 614 |
| | aug-cc-pVTZ | **I** | 7049.3/2023.7/1526.6 | 0 | 0 |
| | | **II** | 10127.4/1494.4/1297.8 | 262 | 328 |
| | | **III** | 14167.6/762.0/734.4 | 725 | 794 |

**Table S2.** The measured transition frequencies $\nu_{obs}$ of isomer I with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit.

| $J''_{ka'\,kc'}$ | $J''_{ka''\,kc''}$ | $F'$ | $F''$ | $\nu_{obs}$/MHz | $\Delta\nu$/kHz |
|---|---|---|---|---|---|
| $2_{02}$ | $1_{01}$ | 3 | 2 | 6849.0241 | 0.5 |
| | | 2 | 1 | 6849.1260 | -0.7 |
| | | 1 | 0 | 6849.4266 | -0.4 |
| $2_{11}$ | $1_{10}$ | 3 | 2 | 7293.0583 | 3.0 |
| | | 2 | 1 | 7293.4990 | -3.7 |
| | | 1 | 0 | 7291.8110 | -1.0 |
| $3_{03}$ | $2_{02}$ | 4 | 3 | 10210.9553 | -0.5 |
| | | 3 | 2 | 10211.0833 | 1.0 |
| | | 2 | 1 | 10211.0358 | 2.7 |
| | | 3 | 3 | 10211.6788 | 5.4 |
| $3_{13}$ | $2_{12}$ | 4 | 3 | 9667.7522 | 0.0 |
| | | 3 | 2 | 9667.9498 | -1.0 |
| | | 2 | 1 | 9667.9162 | 1.4 |
| | | 3 | 3 | 9669.0780 | -1.3 |
| | | 2 | 2 | 9666.1583 | -1.0 |
| $3_{12}$ | $2_{11}$ | 4 | 3 | 10923.1767 | 0.0 |
| | | 3 | 2 | 10923.3154 | 2.3 |
| | | 2 | 1 | 10923.0032 | -1.2 |
| $3_{22}$ | $2_{21}$ | 4 | 3 | 10311.1944 | 4.8 |
| | | 3 | 2 | 10311.7115 | 0.7 |
| | | 2 | 1 | 10310.8948 | -4.2 |
| $3_{21}$ | $2_{20}$ | 4 | 3 | 10411.5180 | 4.0 |
| | | 3 | 2 | 10411.9282 | -1.4 |
| | | 2 | 1 | 10411.2441 | -2.9 |
| $4_{04}$ | $3_{03}$ | 5 | 4 | 13501.1818 | 1.5 |
| | | 4 | 3 | 13501.3339 | 0.7 |
| | | 3 | 2 | 13501.2009 | -6.6 |
| $4_{14}$ | $3_{13}$ | 5 | 4 | 12862.8982 | 0.0 |
| | | 4 | 3 | 12863.0153 | 0.1 |
| | | 3 | 2 | 12862.9914 | 0.0 |
| $4_{13}$ | $3_{12}$ | 5 | 4 | 14532.1909 | -1.5 |
| | | 4 | 3 | 14532.2729 | -2.1 |
| | | 3 | 2 | 14532.1278 | 0.2 |
| $4_{23}$ | $3_{22}$ | 5 | 4 | 13728.4463 | 1.2 |
| | | 4 | 3 | 13728.6850 | 1.2 |
| | | 3 | 2 | 13728.3788 | -4.8 |
| $4_{23}$ | $4_{14}$ | 5 | 5 | 17759.8174 | 0.7 |
| | | 4 | 4 | 17758.6122 | 0.8 |
| | | 3 | 3 | 17760.1292 | 2.6 |
| $4_{22}$ | $3_{21}$ | 5 | 4 | 13975.3409 | 0.9 |
| | | 4 | 3 | 13975.4353 | -2.7 |
| | | 3 | 2 | 13975.2993 | 0.9 |
| $4_{32}$ | $3_{31}$ | 5 | 4 | 13795.7236 | 4.5 |
| | | 4 | 3 | 13796.1701 | -0.7 |
| | | 3 | 2 | 13795.5379 | 0.0 |
| $4_{31}$ | $3_{30}$ | 5 | 4 | 13801.4199 | 4.5 |

| | | | | | |
|---|---|---|---|---|---|
| | | 4 | 3 | 13801.8583 | -2.5 |
| | | 3 | 2 | 13801.2347 | -1.3 |
| $5_{05}$ | $4_{04}$ | 6 | 5 | 16705.7625 | 0.4 |
| | | 5 | 4 | 16705.9341 | -1.1 |
| | | 4 | 3 | 16705.7786 | 4.3 |
| $5_{15}$ | $4_{14}$ | 6 | 5 | 16037.1612 | 0.3 |
| | | 5 | 4 | 16037.2478 | -1.6 |
| | | 4 | 3 | 16037.2222 | 2.2 |
| $5_{14}$ | $4_{13}$ | 6 | 5 | 18110.8291 | -0.1 |
| | | 5 | 4 | 18110.9079 | 3.9 |
| | | 4 | 3 | 18110.7945 | 1.1 |
| $5_{24}$ | $4_{23}$ | 6 | 5 | 17128.6910 | 1.4 |
| | | 5 | 4 | 17128.8346 | 1.7 |
| | | 4 | 3 | 17128.6671 | -6.0 |
| $5_{23}$ | $4_{22}$ | 6 | 5 | 17607.3728 | -0.2 |
| | | 5 | 4 | 17607.3496 | -3.0 |
| | | 4 | 3 | 17607.3728 | 0.2 |
| $5_{33}$ | $4_{32}$ | 6 | 5 | 17261.7744 | 1.2 |
| | | 5 | 4 | 17261.9971 | -1.1 |
| | | 4 | 3 | 17261.7152 | 1.1 |
| $5_{32}$ | $4_{31}$ | 6 | 5 | 17281.6070 | 0.9 |
| | | 5 | 4 | 17281.8192 | 2.7 |
| | | 4 | 3 | 17281.5489 | -0.2 |
| $6_{06}$ | $5_{05}$ | 7 | 6 | 19824.2470 | -0.3 |
| | | 6 | 5 | 19824.4238 | -2.0 |
| | | 5 | 4 | 19824.2467 | -6.7 |
| $6_{16}$ | $5_{15}$ | 7 | 6 | 19188.4417 | 0.9 |
| | | 6 | 5 | 19188.5162 | -0.8 |
| | | 5 | 4 | 19188.4807 | -0.6 |
| $7_{07}$ | $6_{06}$ | 8 | 7 | 22871.4654 | -0.7 |
| | | 7 | 6 | 22871.6372 | 0.7 |
| $7_{17}$ | $6_{16}$ | 8 | 7 | 22316.2818 | -1.5 |
| | | 7 | 6 | 22316.2550 | 1.1 |
| | | 6 | 5 | 22316.3230 | -0.3 |
| $7_{16}$ | $6_{15}$ | 8 | 7 | 25130.2550 | -0.2 |
| | | 7 | 6 | 25130.3500 | -0.9 |
| | | 6 | 5 | 25130.2371 | 1.5 |
| $1_{11}$ | $0_{00}$ | 2 | 1 | 8435.2010 | 1.5 |
| | | 1 | 1 | 8435.7589 | -5.8 |
| | | 0 | 1 | 8434.3510 | -0.4 |
| $2_{12}$ | $1_{01}$ | 3 | 2 | 11453.4518 | 1.0 |
| | | 2 | 1 | 11454.0966 | 5.2 |
| | | 1 | 0 | 11453.5537 | -1.9 |
| $2_{21}$ | $1_{10}$ | 3 | 2 | 22287.1045 | 0.0 |
| | | 2 | 1 | 22287.6307 | -4.3 |
| | | 1 | 0 | 22285.8154 | 0.4 |
| | | 2 | 2 | 22286.5833 | 1.5 |
| | | 1 | 1 | 22288.4471 | -1.1 |
| $2_{20}$ | $1_{11}$ | 3 | 2 | 22731.4232 | -2.0 |
| | | 2 | 1 | 22730.2679 | -1.0 |

| | | | | | |
|---|---|---|---|---|---|
| | | 1 | 0 | 22732.6014 | -0.3 |
| | | 2 | 2 | 22730.8334 | -0.8 |
| | | 1 | 1 | 22731.1899 | 1.4 |
| $2_{20}$ | $2_{11}$ | 2 | 2 | 15019.3113 | 5.1 |
| | | 1 | 1 | 15019.2826 | -0.5 |
| $2_{21}$ | $2_{12}$ | 2 | 2 | 16249.1828 | 1.5 |
| | | 1 | 1 | 16251.7553 | 5.3 |
| $3_{13}$ | $2_{02}$ | 4 | 3 | 14272.1800 | 0.5 |
| | | 3 | 2 | 14272.9153 | -0.1 |
| | | 2 | 1 | 14272.0423 | -1.0 |
| $3_{21}$ | $3_{12}$ | 4 | 4 | 14507.6278 | -0.8 |
| | | 3 | 3 | 14507.9216 | -1.1 |
| | | 2 | 2 | 14507.5259 | 0.2 |
| $3_{22}$ | $3_{13}$ | 4 | 4 | 16894.2696 | -0.1 |
| | | 3 | 3 | 16892.9431 | 0.3 |
| | | 2 | 2 | 16894.7358 | 1.5 |
| $4_{04}$ | $3_{13}$ | 5 | 4 | 9439.9570 | 0.4 |
| | | 4 | 3 | 9439.5005 | 0.5 |
| | | 3 | 2 | 9440.1980 | 0.8 |
| $4_{14}$ | $3_{03}$ | 5 | 4 | 16924.1224 | 0.5 |
| | | 4 | 3 | 16924.8481 | -0.2 |
| | | 3 | 2 | 16924.0004 | -1.2 |
| $4_{22}$ | $4_{13}$ | 5 | 5 | 13950.7767 | 0.5 |
| | | 4 | 4 | 13951.0841 | -1.6 |
| | | 3 | 3 | 13950.6967 | 0.2 |
| $4_{23}$ | $4_{14}$ | 5 | 5 | 17759.8169 | 0.2 |
| | | 4 | 4 | 17758.6115 | 0.1 |
| | | 3 | 3 | 17760.1266 | 0.0 |
| $5_{05}$ | $4_{14}$ | 6 | 5 | 13282.8203 | -1.0 |
| | | 5 | 4 | 13282.4208 | 0.7 |
| | | 4 | 3 | 13282.9821 | 1.9 |
| $5_{15}$ | $4_{04}$ | 6 | 5 | 19460.1027 | 0.2 |
| | | 5 | 4 | 19460.7653 | 0.6 |
| | | 4 | 3 | 19460.0139 | -0.1 |
| $5_{14}$ | $5_{05}$ | 6 | 6 | 9009.5105 | 0.6 |
| | | 5 | 5 | 9008.1561 | 1.1 |
| | | 4 | 4 | 9009.7868 | 0.7 |
| $5_{24}$ | $5_{15}$ | 6 | 6 | 18851.3478 | 2.4 |
| | | 5 | 5 | 18850.1952 | 0.4 |
| | | 4 | 4 | 18851.5701 | -9.6 |
| $5_{23}$ | $5_{14}$ | 6 | 6 | 13447.3198 | 0.0 |
| | | 5 | 5 | 13447.5328 | -1.6 |
| | | 4 | 4 | 13447.2762 | 0.0 |
| $6_{06}$ | $5_{15}$ | 7 | 6 | 17069.9078 | 0.0 |
| | | 6 | 5 | 17069.5970 | 0.5 |
| | | 5 | 4 | 17070.0130 | -0.7 |
| $6_{16}$ | $5_{05}$ | 7 | 6 | 21942.7820 | 1.7 |
| | | 6 | 5 | 21943.3470 | 0.6 |
| | | 5 | 4 | 21942.7210 | 0.0 |
| $6_{15}$ | $6_{06}$ | 7 | 7 | 10833.1812 | -0.6 |

| | | | | | |
|---|---|---|---|---|---|
| | | 6 | 6 | 10831.7312 | 0.9 |
| | | 5 | 5 | 10833.4247 | -2.7 |
| $6_{24}$ | $6_{15}$ | 7 | 7 | 13102.9284 | 3.3 |
| | | 6 | 6 | 13102.9900 | -0.5 |
| | | 5 | 5 | 13102.9105 | -3.2 |
| $7_{07}$ | $6_{16}$ | 8 | 7 | 20752.9315 | -1.7 |
| | | 7 | 6 | 20752.7167 | 0.8 |
| | | 6 | 5 | 20753.0060 | 1.3 |
| $7_{17}$ | $6_{06}$ | 8 | 7 | 24434.7860 | -0.7 |
| | | 7 | 6 | 24435.2441 | 0.1 |
| | | 6 | 5 | 24434.7534 | 2.4 |
| $8_{17}$ | $8_{06}$ | 9 | 9 | 15763.0609 | 2.4 |
| | | 8 | 8 | 15761.4941 | -1.4 |
| | | 7 | 7 | 15763.2550 | 0.2 |

**Table S3.** The measured transition frequencies $\nu_{obs}$ of isomer II with quantum numbers and difference to calculated frequencies $\Delta\nu$ in the least squares fit.

| $J''_{ka' kc'}$ | $J''_{ka'' kc''}$ | $F'$ | $F''$ | $\nu_{obs}$/MHz | $\Delta\nu$/kHz |
|---|---|---|---|---|---|
| $3_{03}$ | $2_{02}$ | 4 | 3 | 8234.0025 | -1.8 |
| | | 3 | 2 | 8234.0543 | -1.7 |
| | | 2 | 1 | 8234.1165 | 2.1 |
| $3_{13}$ | $2_{12}$ | 4 | 3 | 7962.1645 | -2.7 |
| | | 3 | 2 | 7962.3704 | -1.9 |
| | | 2 | 1 | 7962.3310 | 0.2 |
| $3_{12}$ | $2_{11}$ | 4 | 3 | 8526.6786 | -1.5 |
| | | 3 | 2 | 8526.8325 | 9.5 |
| | | 2 | 1 | 8526.5217 | 2.7 |
| $4_{04}$ | $3_{03}$ | 5 | 4 | 10964.1062 | -1.0 |
| | | 4 | 3 | 10964.1582 | -3.2 |
| | | 3 | 2 | 10964.1582 | 2.2 |
| $4_{14}$ | $3_{13}$ | 5 | 4 | 10612.6101 | 1.5 |
| | | 4 | 3 | 10612.7083 | -4.0 |
| | | 3 | 2 | 10612.7083 | 1.1 |
| $4_{13}$ | $3_{12}$ | 5 | 4 | 11365.0509 | -3.7 |
| | | 4 | 3 | 11365.1193 | 0.0 |
| | | 3 | 2 | 11365.0001 | -0.9 |
| $4_{23}$ | $3_{22}$ | 5 | 4 | 10992.5112 | 1.0 |
| | | 4 | 3 | 10992.7730 | 1.7 |
| | | 3 | 2 | 10992.4492 | 6.1 |
| $4_{22}$ | $3_{21}$ | 5 | 4 | 11023.4672 | -2.6 |
| | | 3 | 2 | 11023.4053 | -3.1 |
| $5_{05}$ | $4_{04}$ | 6 | 5 | 13681.8335 | -1.3 |
| | | 5 | 4 | 13681.8934 | -1.5 |
| | | 4 | 3 | 13681.8592 | -2.3 |
| $5_{15}$ | $4_{14}$ | 6 | 5 | 13259.9774 | -0.6 |
| | | 5 | 4 | 13260.0440 | -0.6 |
| | | 4 | 3 | 13260.0440 | 1.8 |
| $5_{14}$ | $4_{13}$ | 6 | 5 | 14200.0126 | 2.4 |
| | | 5 | 4 | 14200.0521 | 1.8 |
| | | 4 | 3 | 14199.9864 | 2.2 |
| $5_{24}$ | $4_{23}$ | 6 | 5 | 13736.5624 | -1.1 |
| | | 4 | 3 | 13736.5432 | -5.4 |
| $5_{23}$ | $4_{22}$ | 6 | 5 | 13798.3159 | 1.8 |
| | | 5 | 4 | 13798.4060 | 0.6 |
| | | 4 | 3 | 13798.3031 | -1.7 |
| $6_{06}$ | $5_{05}$ | 7 | 6 | 16384.3675 | -0.6 |
| | | 6 | 5 | 16384.4360 | 0.4 |
| | | 5 | 4 | 16384.3863 | 2.0 |
| $6_{16}$ | $5_{15}$ | 7 | 6 | 15903.6415 | 1.5 |
| | | 6 | 5 | 15903.6848 | -4.8 |
| | | 5 | 4 | 15903.6848 | 0.1 |
| $6_{15}$ | $5_{14}$ | 7 | 6 | 17030.5815 | 3.5 |
| | | 6 | 5 | 17030.6075 | -1.9 |

| | | | | | |
|---|---|---|---|---|---|
| | | 5 | 4 | 17030.5587 | -3.7 |
| $7_{07}$ | $6_{06}$ | 8 | 7 | 19069.2333 | -1.5 |
| | | 7 | 6 | 19069.3120 | 2.4 |
| | | 6 | 5 | 19069.2457 | 0.4 |
| $7_{16}$ | $6_{15}$ | 8 | 7 | 19855.7072 | 2.4 |
| | | 7 | 6 | 19855.7332 | -0.4 |
| | | 6 | 5 | 19855.6925 | -1.6 |
| $1_{11}$ | $0_{00}$ | 2 | 1 | 11216.8201 | 2.5 |
| | | 1 | 1 | 11217.3150 | -6.3 |
| | | 0 | 1 | 11216.0592 | -2.3 |
| $2_{12}$ | $1_{01}$ | 3 | 2 | 13777.3821 | 0.5 |
| | | 1 | 1 | 13776.1824 | 1.2 |
| $3_{13}$ | $2_{02}$ | 4 | 3 | 16245.0212 | 4.0 |
| | | 3 | 2 | 16245.7429 | -0.9 |
| | | 2 | 1 | 16244.8857 | -5.2 |
| $4_{14}$ | $3_{03}$ | 5 | 4 | 18623.6288 | 7.4 |
| | | 4 | 3 | 18624.4028 | 2.5 |
| | | 3 | 2 | 18623.4802 | -3.5 |

**Table S4**. Partial $r_0$ and B3LYP-G3DBJ /6-311++G(d, p) calculated geometries of isomer I.

| Bond lengths (Å) | | Valence and dihedral angles/° | |
|---|---|---|---|
| C2N1 | 1.356 | | |
| O3C2 | 1.216 | O3C2N1 | 125.0 |
| H4N1 | 1.011 | H4N1C2 | 119.3 |
| H5N1 | 1.006 | H5N1C2 | 121.0 |
| H6C2 | 1.105 | H6C2N1 | 112.9 |
| C7O3 | **2.8363(4)**[a] | C7O3C2 | 121.3 |
| O8C7 | 1.165 | O8C7O3 | **90.22(1)** |
| O9C7 | 1.157 | O9C7O8 | 176.9 |

[a] Error in parentheses in units of the last digit. The parameters in bold have been adjusted to reproduce the experimental values of rotational constants. Their ab initio values are $r$(C7O3) = 2.809 Å, $\alpha$(O8C7O3) = 89.880 ° respectively.

**Table S5**. Partial $r_0$ and B3LYP-G3DBJ /6-311++G(d, p) calculated geometries of isomer II.

| Bond lengths (Å) | | Valence and dihedral angles/° | |
|---|---|---|---|
| C2N1 | 1.357 | | |
| O3C2 | 1.215 | O3C2N1 | 124.6 |
| H4N1 | 1.009 | H4N1C2 | 119.5 |
| H5N1 | 1.104 | H5N1C2 | 121.3 |
| H6C2 | 1.215 | H6C2N1 | 113.1 |
| C7O3 | **2.7886(5)**[a] | C7O3C2 | 111.1 |
| O8C7 | 1.164 | O8C7O3 | **88.785(6)** |
| O9C7 | 1.159 | O9C7O8 | 176.8 |

[a] Error in parentheses in units of the last digit. The parameters in bold have been adjusted to reproduce the experimental values of rotational constants. Their ab initio values are $r$(O3C7) = 2.767 Å, $\alpha$(O8C7O3) = 88.146 ° respectively.

**Table S6**. Intensities (in arbitrary units) of the two isomers for several $\mu_a$-type selected transitions.

| Tranistions | $F'$←$F''$ | conformer | Frequencies | intensities |
|---|---|---|---|---|
| $4_{04}$←$3_{03}$ | 5←4 | I | 13501.1818 | 2.600 |
| | | II | 10964.1062 | 0.132 |
| $4_{14}$←$3_{13}$ | 5←4 | I | 12862.8982 | 1.057 |
| | | II | 10612.6101 | 0.050 |
| $4_{13}$←$3_{12}$ | 5←4 | I | 14532.3909 | 0.800 |
| | | II | 11365.0509 | 0.031 |
| $5_{05}$←$4_{04}$ | 6←5 | I | 16705.7625 | 0.390 |
| | | II | 13681.8335 | 0.068 |
| $5_{15}$←$4_{14}$ | 6←5 | I | 16037.1612 | 0.951 |
| | | II | 13259.9774 | 0.024 |
| $5_{14}$←$4_{13}$ | 6←5 | I | 18110.8291 | 0.668 |
| | | II | 14200.0126 | 0.069 |