**Electronic Supplementary Information**

**On the Synergy of Matrix-Isolation Infrared Spectroscopy
and Vibrational Configuration Interaction Computations**

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| **Table S1: Computed and experimental structural parameters used for the computational assessment.** |
| **Setup** | **Parameter** | **A / GHz** | **B / GHz** | **C / GHz** | **rCO / Å** | **rOH / Å** | **αCOH / °** | **rCH / Å** | **αOCH / °** | **rCH,oop / Å** | **αOCH,oop / °** | **αHCH / °** |
| **S1** | *reBO* | 128.88530 | 24.73180 | 23.89726 | 1.424 | 0.960 | 109.7 | 1.089 | 109.7 | 1.089 | 109.7 |  |
| *rgVSCF(3D)* | 124.39204 | 24.34479 | 23.54341 | 1.435 | 0.960 | 108.4 | 1.100 | 106.8 | 1.106 | 111.9 |  |
| *rgVCI(4)* | 125.06807 | 24.34156 | 23.55778 | 1.435 | 0.951 | 108.8 | 1.100 | 106.9 | 1.106 | 111.8 |  |
| *rgVSCF* | 124.39603 | 24.34267 | 23.54246 | 1.435 | 0.959 | 108.4 | 1.100 | 106.8 | 1.106 | 111.9 |  |
| *rgVCI(5)* | 125.02211 | 24.33724 | 23.55216 | 1.435 | 0.951 | 108.6 | 1.100 | 106.8 | 1.106 | 111.9 |   |
| **S2** | *reBO* | 128.80374 | 24.81405 | 23.97927 | 1.420 | 0.957 | 109.8 | 1.091 | 109.8 | 1.091 | 109.8 |  |
| *rgVSCF(3D)* | 125.26634 | 24.50078 | 23.69142 | 1.429 | 0.957 | 108.7 | 1.098 | 106.9 | 1.105 | 111.9 |  |
| *rgVCI(4)* | 125.88898 | 24.50015 | 23.70765 | 1.429 | 0.949 | 109.0 | 1.098 | 106.9 | 1.104 | 111.9 |  |
| *rgVSCF* | 125.27790 | 24.49560 | 23.68722 | 1.430 | 0.957 | 108.6 | 1.098 | 106.9 | 1.105 | 111.9 |  |
| *rgVCI(5)* | 125.86975 | 24.49235 | 23.69851 | 1.430 | 0.949 | 108.8 | 1.098 | 106.9 | 1.104 | 112.0 |   |
| **S3** | *reBO* | 128.79373 | 24.81156 | 23.97696 | 1.420 | 0.957 | 109.8 | 1.091 | 109.8 | 1.091 | 109.8 |  |
| *rgVSCF(3D)* | 125.29922 | 24.52083 | 23.70823 | 1.429 | 0.957 | 108.7 | 1.099 | 106.9 | 1.104 | 111.9 |  |
| *rgVCI(4)* | 125.99155 | 24.51824 | 23.72403 | 1.429 | 0.948 | 109.0 | 1.098 | 107.0 | 1.104 | 111.9 |  |
| *rgVSCF* | 125.30020 | 24.51924 | 23.70764 | 1.430 | 0.957 | 108.6 | 1.098 | 106.9 | 1.105 | 111.9 |  |
| *rgVCI(5)* | 125.93130 | 24.51465 | 23.71850 | 1.429 | 0.949 | 108.8 | 1.098 | 106.9 | 1.104 | 111.9 |   |
| **S4** | *reBO* | 129.22905 | 24.89401 | 24.05655 | 1.418 | 0.956 | 109.8 | 1.089 | 109.8 | 1.089 | 109.8 |  |
| *rgVSCF(3D)* | 125.71747 | 24.60086 | 23.78708 | 1.426 | 0.956 | 108.8 | 1.097 | 106.9 | 1.103 | 111.9 |  |
| *rgVCI(4)* | 126.41959 | 24.59772 | 23.80254 | 1.435 | 0.951 | 108.8 | 1.100 | 106.9 | 1.106 | 111.8 |  |
| *rgVSCF* | 125.71780 | 24.59945 | 23.78669 | 1.426 | 0.956 | 108.8 | 1.097 | 106.9 | 1.103 | 111.9 |  |
| *rgVCI(5)* | 126.35293 | 24.59502 | 23.79783 | 1.426 | 0.948 | 109.0 | 1.096 | 107.0 | 1.102 | 111.9 |   |
| **S5** | *reBO* | 128.75721 | 24.65181 | 23.82693 | 1.424 | 0.960 | 110.0 | 1.092 | 110.0 | 1.092 | 110.0 |  |
| *rgVSCF(3D)* | 125.52109 | 24.38272 | 23.58429 | 1.432 | 0.959 | 109.5 | 1.099 | 106.9 | 1.106 | 112.0 |  |
| *rgVCI(4)* | 126.33456 | 24.38317 | 23.60606 | 1.431 | 0.950 | 110.1 | 1.099 | 107.0 | 1.099 | 112.0 |  |
| *rgVSCF* | 125.51990 | 24.37868 | 23.58172 | 1.432 | 0.959 | 109.5 | 1.099 | 106.9 | 1.099 | 112.0 |  |
| *rgVCI(5)* | 126.19630 | 24.37353 | 23.59312 | 1.432 | 0.951 | 109.8 | 1.099 | 107.0 | 1.099 | 112.0 |   |
|  |  |  |  |  |  |  |  |  |  |  |  |  |
| Iijima88 [1] | ED & MW, *rz* | 126.37635 | 24.64783 | 23.63020 | 1.428 | 0.975 | 107.6 | 1.098 |   |   |   | 109.1 |
| Herbst84 [2] | MMW & THz, reffective | 127.63075 | 24.68418 | 23.76537 |  |  |  |  |  |  |  |   |
| Benston84 [3] | ED, *ra* |  |  |  | 1.428 | 0.960 |  | 1.096 | 106.8 | 1.102 | 112.6 |   |
| Gerry76 [4] | MW & MMW, *rS* | 127.57103 | 24.68020 | 23.76979 | 1.421 | 0.963 | 108.0 | 1.094 |  |  |  | 108.32 |
| Lees68 [5] | MMW, *rs* |  |  |  | 1.425 | 0.945 | 108.3 | 1.094 |  |  |  | 108.38 |
| Kimura59 [6] | ED |  |  |  | 1.428 | 0.960 | 109.0 | 1.095 |  |  |  | 109.28 |
| Nishikawa56 [7] | MW |  |  |  | 1.427 | 0.953 | 108.2 | 1.096 |  |  |  | 109.4 |
| Swalen55 [8] | MW |  |  |  | 1.428 | 0.967 | 107.2 | 1.098 |  |  |  | 109.6 |
| Venkateswarlu55 [9] | MW |  |  |  | 1.427 | 0.956 | 108.5 | 1.096 |  |  |  | 109.2 |
| Ivash53 [10] | MW |  |  |  | 1.434 | 0.937 | 105.6 | 1.093 |  |  |  | 109.3 |
| **Setup** | **Parameter** | **A / GHz** | **B / GHz** | **C / GHz** | **rCO / Å** | **rOH / Å** | **αCOH / °** | **rCH / Å** | **αOCH / °** | **rCH,oop / Å** | **αOCH,oop / °** | **αHCH / °** |

**Structural parameters calculated for methanol with various setting**

Table S1 comprises structural parameters (rotational constants, bond lengths and angles). We distinguish between Born-Oppenheimer equilibrium parameters (re) and vibrationally-averaged structural parameters (*rg*). The data used in the evaluation is highlighted blue.

**References**

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