Cost-Effective Quantum Mechanical Approach for Predicting Thermodynamic and Mechanical Stability of Pure-Silica Zeolites

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Supporting Information
Computational details

Table S1. Shrinking factor used in all calculations.

| NAME | HF-3c // B3LYP/SVP and VTZP // PBE/VTZP | PBEh-3c |
|------|------------------------------------------|---------|
| FAU  | 2 2                                      | 2 2     |
| ISV  | 2 2                                      | 2 2     |
| AFI  | 4 4                                      | 4 4     |
| AST  | 2 2                                      | 4 4     |
| FER  | 2 2                                      | 4 4     |
| MEL  | 2 2                                      | 4 4     |
| CFI  | 4 4                                      | 4 4     |
| CHA  | 2 2                                      | 6 6     |
| IFR  | 2 2                                      | 6 6     |
| ITE  | 2 2                                      | 6 6     |
| MTW  | 4 4                                      | 6 6     |
| MWW  | 2 2                                      | 6 6     |
| MFI  | 2 2                                      | 2 2     |
| STT  | 2 2                                      | 2 2     |
| QUA  | 6 6*                                     | 8 8     |

*10 10 in the B3LYP/VTZP case

Table S2. TOLINTEGR values used in the calculations.

| TOLINTEGR | B3LYP/SVP and VTZP | HF-3c | PBEh-3c | PBE/VTZP |
|-----------|---------------------|-------|---------|----------|
| T1        | 8 7 7 7 25          | 7 7 7 18 | 7 7 9 30 | 6 6      |
| T2        |                     |       |         |          |
| T3        |                     |       |         |          |
| T4        |                     |       |         |          |
| T5        |                     |       |         |          |

Statistical functions adopted in the paper

\[
\text{MAE} = \frac{1}{N} \cdot \sum |\delta_i|, \quad \text{MARE} = \frac{1}{N} \cdot \sum |\delta_i|\% \quad \delta_i = |x_i| - |x_i^{\text{exp}}|, \quad \delta_i\% = 100 \cdot \frac{|x_i| - |x_i^{\text{exp}}|}{|x_i^{\text{exp}}|} \quad \text{ME} = \frac{1}{N} \cdot \sum |\delta_i|
\]

\[
, \quad \text{MRE} = \frac{1}{N} \cdot \sum |\delta_i|\% , \quad SD = \sqrt{\frac{\Sigma (\delta_i - \bar{\delta})^2}{N - 1}} , \quad SD\% = \sqrt{\frac{\Sigma (\delta_i - \bar{\delta})^2}{N - 1}} \quad \text{with } i=1, \ldots, N,
\]

\[
P = \frac{\Sigma (x_i - \bar{x})(y_i - \bar{y})}{\Sigma (x_i - \bar{x})^2(y_i - \bar{y})^2}
\]
## Basis sets

**B3LYP SVP basis set**

14 5
0 0 8 2 0 1.0
149866.0  0.0001215
22080.6   0.0009770
4817.5    0.0055181
1273.5    0.0252000
385.11    0.0926563
128.429   0.2608729
45.4475   0.4637538
16.2589   0.2952000
0 1 8 8 0 1.0
881.111  -0.0003   0.0006809
205.84    -0.0050   0.0059446
64.8552   -0.0368   0.0312000
23.9     -0.1079   0.1084000
10.001    0.0134   0.2378000
4.4722    0.3675   0.3560066
1.0780    0.0050   0.0059446
0 1 3 4 0 1.0
2.6668   -0.0491   0.0465000
1.0780   -0.1167  -0.1005000
0.3682   0.2300  -1.0329000
0 1 1 0 1.0
0.193    1.0      1.0
0 3 1 0 1.0
0.610    1.0
8 5
0 0 8 2 0 1.0
8966.29   0.0010
1240.17   0.0091
252.114   0.0513
70.359    0.1702
23.9025   0.3662
9.2075    0.3859
3.9847    0.1471
1.2266    0.0695
0 1 4 6 0 1.0
44.9344  -0.0098   0.0107
10.3978  -0.0893   0.0670
3.2970   -0.0373   0.2100
1.2340    0.3730   0.3542
0 1 1 0 1.0
0.4536   1.0      1.0
0 1 1 0 1.0
0.1810   1.0      1.0
0 3 1 0 1.0
0.60     1.0

**B3LYP and PBE VTZP basis set**

14 13
0 0 5 2 0 1.0
79079.4340000  0.26431386E-03
11855.0100000  0.20485143E-02
2697.7051000   0.10637241E-01
762.8722700 0.43082477E-01
247.2845500 0.13898279
0 0 1 2.0 1.0
87.9312400 1.000000
0 0 2 2.0 1.0
33.8232840 0.44071543
13.8681080 0.20091165
0 0 1 0.0 1.0
3.9920017 1.000000
0 0 1 0.0 1.0
1.4659925 1.000000
0 0 1 0.0 1.0
0.25271086 1.000000
0 0 1 0.0 1.0
0.92491673E-01 1.000000
0 2 5 6.0 1.0
483.2035200 0.19161547E-02
114.2508100 0.15309765E-01
36.3877860 0.71094358E-01
13.4117040 0.21243244
5.2884033 0.38976302
0 2 1 2.0 1.0
2.1374219 1.000000
0 2 1 0.0 1.0
0.86468463 1.000000
0 2 1 0.0 1.0
0.25489855 1.000000
0 2 1 0.0 1.0
0.79397031E-01 1.000000
0 3 1 0.0 1.0
0.3500000 1.000000
8 10
0 0 5 2.0 1.0
15902.6474590 0.51499803703E-03
2384.9537829 0.39819764428E-02
542.71957182 0.20476971922E-01
153.40407874 0.80262367915E-01
49.545716140 0.23766839947
0 0 1 2.0 1.0
17.339649897 1.000000
0 0 1 0.0 1.0
6.3303355272 1.000000
0 0 1 0.0 1.0
1.6995882201 1.000000
0 0 1 0.0 1.0
0.68954491271 1.000000
0 0 1 0.0 1.0
0.23936028181 1.000000
0 2 4 4.0 1.0
63.270524011 0.60709205960E-02
14.623312295 0.41947688723E-01
4.4489518003 0.16156883988
1.5281513180 0.35682779292
0 2 1 0.0 1.0
0.52997315870 1.000000
0 2 1 0.0 1.0
0.17509445998 1.000000
0 3 1 0.0 1.0
1.2000000 1.000000
Results and Discussion

Table S3. Zeolite optimized volume at the B3LYP-D2/VTZP, PBE-D2/VTZP, PBE0-D2/VTZP, HF-3c, HF-3c-027 and PBEh-3c levels of theory. Results in cm$^3$ mol$^{-1}$ per SiO$_2$ unit.

| name  | exp  | B3LYP-D2 VTZP | PBE0-D2 VTZP | PBE-D2 VTZP | HF-3c | HF-3c-027 | PBEh-3c |
|-------|------|---------------|--------------|-------------|-------|-----------|---------|
| AFI   | 33.83| 36.79         | 36.41        | 37.06       | 33.81 | 34.01     | 35.97   |
| AST   | 34.83| 39.63         | 39.22        | 40.19       | 35.71 | 35.89     | 38.76   |
| CFI   | 32.94| 37.53         | 37.15        | 37.98       | 34.03 | 34.24     | 36.69   |
| CHA   | 39.10| 41.43         | 39.68        | 39.42       | 37.85 | 38.07     | 40.59   |
| FAU   | 44.77| 47.53         | 46.97        | 47.61       | 43.67 | 43.95     | 46.17   |
| FER   | 32.67| 35.57         | 35.22        | 36.04       | 32.18 | 32.37     | 34.78   |
| IFR   | 35.36| 36.37         | 36.10        | 36.28       | 34.43 | 34.74     | 35.52   |
| ISV   | 39.21| 41.46         | 41.01        | 41.64       | 38.44 | 38.69     | 40.59   |
| ITE   | 37.04| 38.56         | 38.19        | 38.38       | 36.13 | 36.37     | 37.40   |
| MEL   | 33.83| 35.87         | 35.80        | 35.70       | 33.35 | 33.57     | 34.76   |
| MFI2  | 33.51| 34.43         | 34.21        | 34.37       | 33.22 | 33.45     | 33.29   |
| MTW   | 31.06| 34.57         | 34.29        | 35.00       | 32.15 | 32.35     | 33.48   |
| MWW   | 36.47| 39.22         | 38.81        | 39.63       | 35.75 | 35.98     | 38.33   |
| STT   | 35.78| 37.29         | 36.97        | 37.08       | 35.16 | 35.42     | 36.09   |
| QUARTZ| 22.71| 22.47         | 22.54        | 22.67       | 23.22 | 23.41     | 22.44   |
Table S4. Calculated and experimental energy and enthalpy of formation of zeolites with respect to α-quartz in kJ·mol⁻¹ per SiO₂ unit. B refers to B3LYP. P refers to PBE.

| Zeolite | ΔH | ±Δ | ZPE (HF-3c-027) SCALED | E₂ 298.15K(HF-3c-027) | ΔE (quasi-exp.) |
|---------|----|----|------------------------|------------------------|-----------------|
| AFI     | 7.2| 0.9| 1.2                    | 1.2                    | 4.9             |
| AST     | 10.9| 1.2| 1.0                    | 0.9                    | 9.0             |
| CFI     | 8.8| 0.8| 0.8                    | 1.1                    | 6.8             |
| CHA     | 11.4| 1.5| 1.3                    | 0.8                    | 9.3             |
| FAU     | 13.6| 0.7| 1.5                    | 1.2                    | 11.0            |
| FER     | 6.6 | 1.0| 1.2                    | 1.2                    | 4.3             |
| IFR     | 10.0| 1.2| 1.3                    | 1.0                    | 7.7             |
| ISV     | 14.4| 1.1| 1.4                    | 1.1                    | 11.9            |
| ITE     | 10.1| 1.2| 1.3                    | 1.2                    | 7.5             |
| MEL     | 8.2 | 1.3| 1.3                    | 1.4                    | 5.6             |
| MFI2    | 6.8 | 0.8| 1.1                    | 1.0                    | 4.7             |
| MTW     | 8.7 | 0.8| 0.8                    | 1.3                    | 6.5             |
| MWW     | 10.4| 1.5| 1.4                    | 1.3                    | 7.7             |
| STT     | 9.2 | 1.2| 1.3                    | 1.0                    | 6.9             |

| Zeolite | SP-P/VTZP-D3ABCD | SP-P/VTZP-D2 | SP-Ph-3c | SP-B/SVP-D* | SP-B/SVP-D3ABCD | SP-B-D*/VTZP | SP-B-D3ABCD/VTZP |
|---------|------------------|-------------|---------|------------|---------------|-------------|------------------|
| AFI     | 5.2              | 4.5         | 6.7     | 10.5       | 14.0          | 6.4         | 9.8              |
| AST     | 9.6              | 8.6         | 10.9    | 13.1       | 17.5          | 10.2        | 14.6             |
| CFI     | 6.4              | 5.8         | 7.4     | 11.6       | 15.2          | 7.4         | 10.9             |
| CHA     | 8.3              | 7.1         | 10.0    | 12.6       | 17.0          | 9.9         | 14.4             |
| FAU     | 9.8              | 8.4         | 11.3    | 14.0       | 18.3          | 11.6        | 15.9             |
| FER     | 4.5              | 3.9         | 6.2     | 8.7        | 11.8          | 5.4         | 8.5              |
| IFR     | 5.9              | 5.1         | 8.0     | 10.3       | 13.5          | 7.7         | 10.9             |
| ISV     | 8.9              | 7.8         | 10.5    | 13.1       | 16.7          | 10.4        | 14.0             |
| ITE     | 6.5              | 5.7         | 8.3     | 11.2       | 15.1          | 7.9         | 11.8             |
| MEL     | 4.8              | 4.2         | 6.2     | 9.2        | 12.4          | 5.8         | 9.1              |
| MFI2    | 4.6              | 4.0         | 5.9     | 9.0        | 12.2          | 5.5         | 8.7              |
| MTW     | 4.7              | 4.2         | 5.7     | 9.4        | 12.7          | 5.5         | 8.8              |
| MWW     | 6.8              | 5.9         | 8.2     | 10.3       | 13.6          | 7.8         | 11.0             |
| STT     | 7.2              | 6.3         | 8.8     | 11.7       | 15.4          | 8.4         | 12.1             |

| Zeolite | B-D2/VTZP | PO-D2/VTZP | HF-3c | HF-3c-027 | Ph-3c | P/VTZP-D2 |
|---------|------------|------------|-------|-----------|-------|-----------|
| AFI     | 15.6       | 11.6       | 14.5  | 10.6      | 14.4  | 14.3      |
| AST     | 19.9       | 15.2       | 18.8  | 14.2      | 19.4  | 19.3      |
| CFI     | 16.5       | 12.5       | 14.2  | 10.0      | 16.1  | 16.0      |
| CHA     | 19.3       | 14.0       | 21.7  | 17.6      | 17.0  | 16.1      |
| FAU     | 20.6       | 15.4       | 25.6  | 21.9      | 17.1  | 17.3      |
| FER     | 14.7       | 10.9       | 13.0  | 9.4       | 14.2  | 14.2      |
| IFR     | 15.6       | 11.6       | 19.4  | 16.3      | 13.2  | 12.8      |
| ISV     | 18.8       | 14.3       | 20.6  | 17.2      | 17.3  | 16.6      |
| ITE     | 16.4       | 12.0       | 18.4  | 14.4      | 14.3  | 14.0      |
| MEL     | 14.3       | 10.6       | 13.4  | 9.6       | 12.9  | 13.1      |
| MFI2    | 13.2       | 9.5        | 12.6  | 8.7       | 11.2  | 12.0      |
| MTW     | 13.9       | 10.2       | 11.8  | 7.8       | 13.0  | 13.3      |
| MWW     | 16.7       | 12.5       | 17.8  | 14.4      | 15.6  | 15.4      |
| STT     | 16.5       | 12.2       | 18.3  | 14.5      | 14.6  | 14.3      |
Figure S1 Correlation between dispersion energy as computed with both D* and D3 corrections (to the PBE functional) and the density of the SiO₂ polymorphs.
Figure S2 IR spectra of the zeolite set at the HF-3c-027 level of theory.

Table S5. Statistical analysis (in %) of the calculated mechanical properties of zeolites at the HF-3c and HF-3c-027 levels with respect to B3LYP/SVP-D2, taken from Ref. 4.

| E and G components | ME | MARE | SD |
|--------------------|----|------|----|
| Emin               | 18 | 18   | 13 |
| Emax               | 31 | 31   | 9  |
| Gmin               | 16 | 20   | 19 |
| Gmax               | 34 | 34   | 21 |

| HF-3c-027          |    |      |    |
|--------------------|----|------|----|
| Emin               | 28 | 29   | 16 |
| Emax               | 35 | 35   | 12 |
| Gmin               | 22 | 26   | 22 |
| Gmax               | 38 | 38   | 20 |
Table S6. Minimum and maximum values for the Young's modulus (E) and shear modulus (G) values for the zeolite set.

| Zeolite | Emin (GPa) | Emax (GPa) | Gmin (GPa) | Gmax (GPa) |
|---------|------------|------------|------------|------------|
| **B3LYP/SVP-D2** | | | | |
| AFI   | 84.7       | 182.1      | 32.8       | 50.4       |
| AST   | 28.4       | 97.4       | 9.8        | 36.2       |
| CFI   | 78.6       | 116.9      | 25.5       | 39.5       |
| CHA   | 19.1       | 80.8       | 8.3        | 30.5       |
| FAU   | 45.7       | 53.2       | 16.6       | 19.6       |
| FER   | 67.0       | 162.1      | 26.0       | 48.2       |
| IFR   | 41.2       | 95.4       | 17.1       | 37.5       |
| ITE   | 43.1       | 81.5       | 13.3       | 35.9       |
| MTW   | 44.5       | 108.1      | 14.4       | 54.4       |
| **HF-3c** | | | | |
| AFI   | 86.3       | 234.7      | 27.2       | 60.2       |
| AST   | 35.7       | 124.2      | 12.4       | 46.3       |
| CFI   | 93.9       | 151.3      | 31.9       | 65.4       |
| CHA   | 25.3       | 102.9      | 11.7       | 39.1       |
| FAU   | 58.6       | 64.9       | 21.4       | 23.9       |
| FER   | 83.1       | 207.8      | 25.4       | 84.8       |
| IFR   | 42.8       | 119.7      | 17.6       | 47.8       |
| ITE   | 55.7       | 115.3      | 17.5       | 43.9       |
| MTW   | 45.2       | 161.0      | 15.0       | 64.8       |
| **HF-3c-027** | | | | |
| AFI   | 96.7       | 233.7      | 31.2       | 62.7       |
| AST   | 39.8       | 122.6      | 13.3       | 46.6       |
| CFI   | 99.8       | 153.2      | 33.9       | 66.6       |
| CHA   | 28.2       | 105.9      | 12.8       | 40.3       |
| FAU   | 59.4       | 67.6       | 21.7       | 25.0       |
| FER   | 87.3       | 209.1      | 27.3       | 85.5       |
| IFR   | 53.0       | 125.7      | 20.1       | 49.3       |
| ITE   | 59.0       | 120.1      | 18.6       | 45.4       |
| MTW   | 41.3       | 174.4      | 12.7       | 67.9       |
Figure S3 Emin, Emax, Gmin and Gmax computed at the HF-3c and HF-3c-027 levels of theory.

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