

Toward a Database of Hypothetical Zeolite Structures

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We present a computational method to identify zeolite-like frameworks by sampling a zeolite figure of merit. Monte Carlo methods, including simulated annealing, are used to perform the sampling. We discuss construction of a database of hypothetical zeolite frameworks with this approach and discuss how the database may be used to search for new zeolite structures with specific material properties of interest.

1. Introduction

Zeolite materials have found a wide range of uses in industrial applications. They are used as catalysts, molecular sieves, and ion-exchangers.^{1–5} Classical zeolites are aluminosilicates. The basic building block is a TO₄ tetrahedron. Usually T = Si, although substitution of the silicon with aluminum, phosphorus, or other metals is common. A key current limitation in the discovery of new zeolites with optimized properties is our lack of fundamental understanding of the zeolite nucleation and crystallization process. Important correlations between structure-directing templates and the resulting zeolite material have been made, and experimentally motivated hypotheses about the fundamental nucleation events have been put forward. A complete understanding of the crystallization pathway, however, has not been achieved.

To date, the International Zeolite Association (IZA) Structure Commission recognizes the existence of 165 different topologies for zeolite structures.⁶ We may ask ourselves if this number represents a near upper limit on the possible zeolite topologies that may exist in nature or are possible to synthesize in the laboratory. The answer is almost certainly no, as evidenced by the recent discoveries of a number of new topologies including EON,^{7,8} NSI,⁹ and OWE.¹⁰ If the answer is indeed no, then what are the additional structures that may exist, and how can one synthesize them? We use theory and computation to answer the first question by developing a database of hypothetical topologies. There is a tremendous demand for novel zeolite structures with novel properties. Such a database might be of great use to fuel the imagination of synthetic solid-state chemists in their search for these new structures.

If we assume that the production of a database of potential topologies is feasible, then how might one use such a database? We believe one of the most fruitful uses of such a database would be to search it for materials with useful properties. If one were interested in structural properties, for example, the size of rings in a structure and the dimensions of channels, then such a search would be easy to perform. If, however, the property of interest were functional, for example, a catalytic property, then the search would be more problematic. A direct quantum calculation is difficult and time-consuming. One can search, however, for constraints on the possible catalytic reactions a material might facilitate by looking at reactant, transition state, and product selectivities.^{11–13} Once a structure

or group of structures has been identified as being potentially useful, one still needs to synthesize the zeolite or zeolites in question. This is very difficult, but progress is possible through a better understanding of the nucleation event¹⁴ and with template molecule prediction methods.¹⁵

The history of the method that we use to search for hypothetical structures goes back to the late 1980s when the program zefsa was developed.^{16,17} The program zefsa solves zeolite structures from X-ray powder diffraction data. It can also, however, produce hypothetical structures if diffraction data are not included. Using this program 2000 hypothetical structures were produced.¹⁷ This number can be compared to the hundreds of structures developed at that time by hand from physical model building by J. V. Smith. In 2003, the program zefsaII was used to generate 2000 new hypothetical structures from the unit cells and symmetries of the publicly known zeolite structures.¹⁸ Also at this time, the ring histograms of most of the known zeolite topologies from the IZA Structure Commission Atlas and the hypothetical structures were calculated and compared.¹⁸ The zefsaII method is now one of the standard methods for solving new zeolite structures from powder diffraction data and has been for roughly a decade.¹⁹ Roughly a dozen zeolite structures have been solved with this method.²⁰ This powerful, biased Monte Carlo approach can determine the structure of a new zeolitic material from the powder diffraction pattern and density, both of which are easily measured in experiments. All of the publicly known zeolites were solved in a realistic test application of the method.¹⁹ The method is rapid and automatic, making it a natural tool for use within the combinational chemistry paradigm.

Since the middle of 2004, we have been generating hypothetical topologies using the systematic computational approach that we describe in section 2. To date, approximately one million new topologies have been found. In section 3, we summarize the results of the search so far. In section 4, we discuss the future of the database and how one might refine the topologies found to include only thermodynamically accessible structures. We conclude in section 5.

2. Construction of the Database

There exist 230 different crystallographic space groups, and any periodic crystal structure can be constructed from a unit cell with a particular size, shape, density of atoms, number of crystallographically unique atoms, and space group symmetry. We have developed a systematic computational procedure to search through unit cells with different space group symmetries. We use Monte Carlo methods to explore the space of possible

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zeolite structures. For each space group, we explore the range of possible unit cell sizes (a , b , c , α , β , γ). For many of the 230 possible space groups, there are constraints on the possible values of the unit cell parameters. Within these constraints, we vary a , b , and c from 3 to 30 Å in steps of 3 Å. Since the distance between Si atoms in zeolites is about 3.1 Å, a unit cell with a dimension smaller than 3 Å is impossible. We use a step size of 3 Å, also because this is the approximate distance required to insert a new Si atom and to create a new structure. We explore the allowed angle values in steps of 10°. This value is chosen because $30 \text{ Å} \times \pi \times 10/180 \approx 5.3 \text{ Å}$, a distance displacement for the largest unit cells roughly equal to the step size of 3 Å. We vary the T atom density from 12 to 20 in steps of 2 per 1000 Å³, since the typical zeolite density is in the range of 14 to 18 T atoms per 1000 Å³. These density numbers are taken as the extremes observed in the IZA Structure Commission Atlas of zeolite structures.⁶ We vary the number of unique T atoms in the unit cell from a value of $n_{\text{tot}}/n_{\text{sym}}$ (where n_{tot} = total number of T atoms in unit cell and n_{sym} = number of symmetry operators) to $4.5n_{\text{tot}}/n_{\text{sym}}$. The number 4.5 is calculated as 1.5 times the largest ratio of $n_{\text{tot}}/n_{\text{sym}}$ from the IZA Structure Commission Atlas⁶ and is, thus, conservative. We limit the total number of unique T atoms to less than or equal to 8, as larger numbers of unique T atoms require significantly more expensive (by at least a factor of 10) parallel tempering methods to solve the structures reliably.¹⁹ While it is possible for zefsall to easily solve zeolite structures with greater than 8 unique T atoms when powder diffraction data are available, it is not easy to fully populate the database with all possible hypothetical structures with greater than 8 unique T atoms.

For each unit cell produced using the above criteria, we conduct 100 zefsall biased Monte Carlo simulated annealing runs. The energy of a postulated configuration of T atoms in the zeolite is represented by a zeolite figure of merit, defined by¹⁹

$$H = \alpha_{\text{T-T}} H_{\text{T-T}} + \alpha_{\text{T-T-T}} H_{\text{T-T-T}} + \alpha_{\langle \text{T-T-T} \rangle} H_{\langle \text{T-T-T} \rangle} + \alpha_{\text{D}} H_{\text{D}} + \alpha_{\text{M}} H_{\text{M}} + \alpha_{\text{UC}} H_{\text{UC}} + \alpha_{\text{NB}} H_{\text{NB}} \quad (1)$$

The different contributions to eq 1 are of two types: the geometric terms and the density terms. The first three terms, which are geometric, are obtained by histogramming the T–T distances and the T–T–T angles of 32 known high silica zeolites.^{17,21} The T–T distance is sharply distributed around 3.1 Å, and the T–T–T angles are distributed around 109.5°, as one would expect for a tetrahedrally coordinated species.¹⁹ The angle $\langle \text{T-T-T} \rangle$ is the average of all of the angles around a given T atom. The H_{NB} and H_{UC} terms account for the 4-connectedness of silicates. These terms are defined to be nonzero and positive whenever a T atom happens to have greater than or fewer than four first neighbors, respectively, where a neighbor is defined as an atom closer than 4 Å. If the number of neighbors is fewer than four, we simply assign a progressively larger weight to the atom. The H_{M} term favors merging. Merging occurs in crystals whenever a particular atom sits on a special position, a position invariant under one or more symmetry operations other than the identity. Since our method assigns positions in a stochastic way, it is unlikely that we would find an atom exactly on a special position. Therefore, we define a merging range with a typical value of $r_{\text{M}} = 0.8 \text{ Å}$. Two or more symmetry-related atoms that fall within this distance are merged. To enforce the density, we include the term

$$H_{\text{D}} = (n_{\text{T}} - n_0)^2 \quad (2)$$

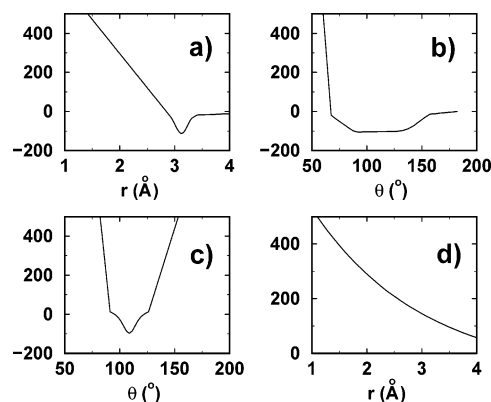


Figure 1. (a) T–T potential energy, (b) T–T–T angle potential energy, (c) $\langle \text{T-T-T} \rangle$ average angle potential energy, and (d) repulsive potential energy for nonbonded neighbors. After ref 19.

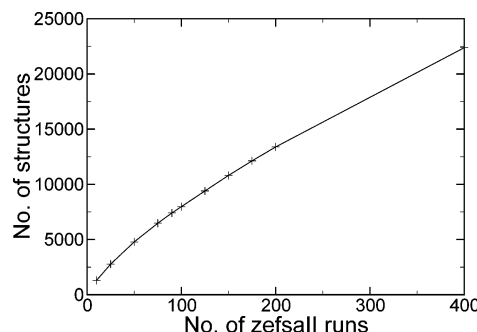


Figure 2. Number of structures found as a function of the number of simulated annealing runs used per unit cell. Data are taken from space group 91.

where n_{T} is the actual number of atoms in the unit cell after merging and n_0 is the number of T atoms expected from the input density specified for the run. The α_i terms weight the different contributions to the figure of merit. These weights have been optimized to solve real structures of zeolites in the shortest number of runs, and they are kept fixed for all the simulations we perform. The forms of the main terms in the zeolite figure of merit are shown in Figure 1. In each run, the only variables are the positions of the T atoms in the unit cell. Full details of the figure of merit can be found elsewhere.¹⁹

Each zefsall run has a different random number seed. The output for each unit cell is initially analyzed to remove all structures with identical connectivities, as defined by the coordination sequence out to 12 atoms. The figure of merit of a structure must be favorable (negative) to survive analysis, as all publicly known zeolite structures have a negative figure of merit. All the structures from all the different unit cells are then collated, and structures with identical connectivities are removed. This procedure ensures that only the structures with the lowest energy per number of T atoms for a given connectivity are added to the database for a given space group. Unique T atoms in the same structure with identical connectivities are considered to be one T atom in this analysis.

How good a coverage of hypothetical zeolite structures does our method achieve? By simply increasing the number of simulated annealing runs, one can increase the number of structures found. In Figure 2, we plot the number of structures found as a function of the number of simulated annealing runs performed for a typical space group. Shown in Figure 3 are the number of structures found from the method for a typical space group, as a function of the value of the figure of merit per tetrahedral atom, and the number of simulated annealing runs performed. One observes that the number of structures with a

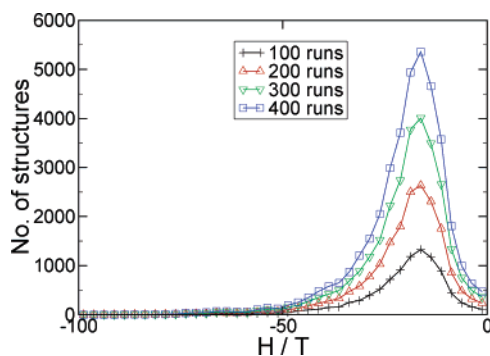


Figure 3. Number of structures found as a function of the figure of merit of the structures, for different numbers of simulated annealing runs used per unit cell. Data is taken from space group 91.

Table 1. Number of Structures Found in the Orthorhombic Space Groups

space group	no. of unit cells	no. unique structures
16	3186	9705
17	3186	11268
18	3186	9676
19	3186	7609
20	6707	31398
21	6707	39663
36	6707	17433
63	8825	74564

favorable (low) figure of merit score converges reasonably quickly, whereas the total number of structures found as a function of the number of runs converges more slowly. We note, however, that the procedure we use is capable of solving 86% of publicly known zeolite structures,¹⁷ so we are confident of finding most structures of interest for a particular unit cell, at least for the smaller numbers of unique T atoms per unit cell. It is apparent that if the computational resources were available, we could find 2–4 times as many structures, although with the 100 runs that we perform we find many, but not all, of the very good structures. We choose 100 runs because increasing the computational resources by X times yields rather less than X times more structures. We also note that, by decreasing the step size in the search through unit cell volumes, we would find additional structures, again at a significantly increased computational expense.

It is interesting to compare our sampling-based procedure with enumeration-based methods.^{22–24} Enumeration methods list all possible structures, whereas our sampling procedure generates results with favorable structures. In addition, for large numbers of unique tetrahedral atoms, enumeration generates too many structures for practical use, most of which have very unfavorable energies. Sampling and enumeration approaches, however, are complementary. We opt for sampling so as to produce mostly thermodynamically accessible structures.

3. Results

To date, we have completed our search protocol for all the tetragonal (nos. 75–142), trigonal (nos. 143–167), hexagonal (nos. 168–194), and cubic (nos. 195–230) space groups and for some of the orthorhombic ones. The results from our search procedure are constantly updated on the web.²⁵ In Tables 1–5, is a summary of our results showing the number of unit cells searched and the number of acceptable unique structures found for each space group. The database currently contains approximately one million structures, and structures can be accessed according to their space group symmetry, lattice parameters, and number of unique tetrahedral atoms in the unit

Table 2. Number of Structures Found in the Tetragonal Space Groups

space group	no. of unit cells	no. unique structures
75	234	771
76	234	1717
77	234	1768
78	234	1760
79	503	2204
80	503	2700
81	234	1925
82	503	4145
83	503	3542
84	503	5923
85	503	2500
86	503	5299
87	699	6774
88	699	6642
89	503	3067
90	503	3145
91	503	7978/22537 ^a
92	503	4611
93	503	7883
94	503	5702
95	503	8075
96	503	4581
97	699	8226
98	699	12170
99	503	2352
100	503	1550
101	503	3077
102	503	3703
103	503	1625
104	503	2015
105	503	5001
106	503	1783
107	699	6326
108	699	3580
109	699	5801
110	699	3312
111	503	4468
112	503	6407
113	503	1994
114	503	4061
115	503	6337
116	503	5366
117	503	3561
118	503	6957
119	699	10582
120	699	6732
121	699	8485
122	699	9749
123	699	8895
124	699	7357
125	699	6693
126	699	6685
127	699	6695
128	699	7450
129	699	8035
130	699	5015
131	699	13967
132	699	11111
133	699	8118
134	699	11746
135	699	6919
136	699	10051
137	699	10778
138	699	8319
139	802	14789
140	802	11878
141	802	14652
142	802	13788

^a From 400 zefsaII runs.

cell. In the future, we will implement search procedures based on ring size and channel dimensions.

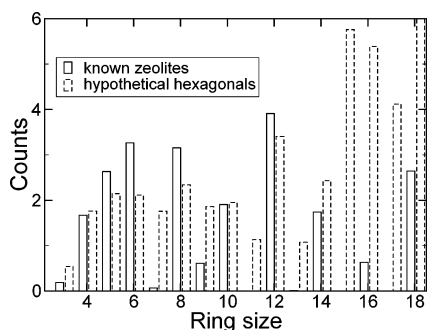
It is of interest to compare the publicly known zeolite topologies with the hypothetical structures that we have

Table 3. Number of Structures Found in the Trigonal Space Groups

space group	no. of unit cells	no. unique structures
143	135	257
144	135	1068
145	135	1047
146	463	2359
147	344	1139
148	694	4082
149	344	1178
150	344	1175
151	344	5096
152	344	3774
153	344	5249
154	344	3845
155	694	8581
156	344	1156
157	344	690
158	344	790
159	344	1320
160	694	4713
161	694	2476
162	589	4121
163	589	4442
164	589	5676
165	589	3377
166	769	10873
167	769	7295

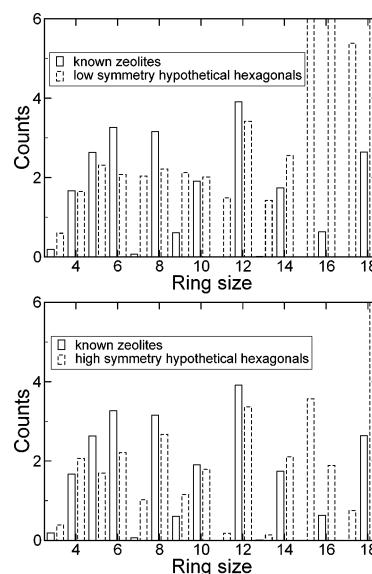
Table 4. Number of Structures Found in the Hexagonal Space Groups

space group	no. of unit cells	no. unique structures
168	344	492
169	344	1902
170	344	1959
171	847	6166
172	344	3023
173	344	1521
174	344	1108
175	589	3417
176	589	4559
177	589	3322
178	589	9717
179	589	9679
180	589	12484
181	589	12487
182	589	5814
183	589	3234
184	589	1421
185	589	2237
186	589	4446
187	589	4690
188	589	4578
189	589	3762
190	589	5209
191	758	10933
192	758	7304
193	758	9444
194	758	12508

**Figure 4.** Ring size distribution in known zeolites compared to all hexagonal structures in the hypothetical database.**Table 5. Number of Structures Found in the Cubic Space Groups**

space group	no. of unit cells	no. unique structures
195	47	502
196	76	538
197	66	782
198	47	446
199	66	758
200	66	710
201	66	803
202	76	499
203	76	672
204	76	707
205	66	610
206	76	641
207	66	553
208	66	1191
209	76	734
210	76	727
211	76	852
212	66	713
213	66	735
214	76	795
215	66	1053
216	76	1075
217	76	803
218	66	798
219	76	579
220	76	574
221	76	940
222	76	594
223	76	964
224	76	901
225	76	365
226	76	368
227	76	1170
228	76	740
229	76	1039
230	76	770

produced. Shown in Figure 4 is the frequency of ring sizes found in known structures compared to all of the hexagonal structures from the database. The hypothetical structures have a fairly similar ring size distribution to the known structures. Interestingly, we predict that more structures with 16 tetrahedral atom rings may exist than are currently found. Previously, a similar analysis was performed comparing the publicly known structures as of the year 1998 with 2000 hypothetical structures.¹⁸ Since that time, a large number of new, known zeolite structures have

**Figure 5.** Ring size distribution in known zeolites compared to that in low- (top) and high-symmetry (bottom) hexagonal structures in the hypothetical database.

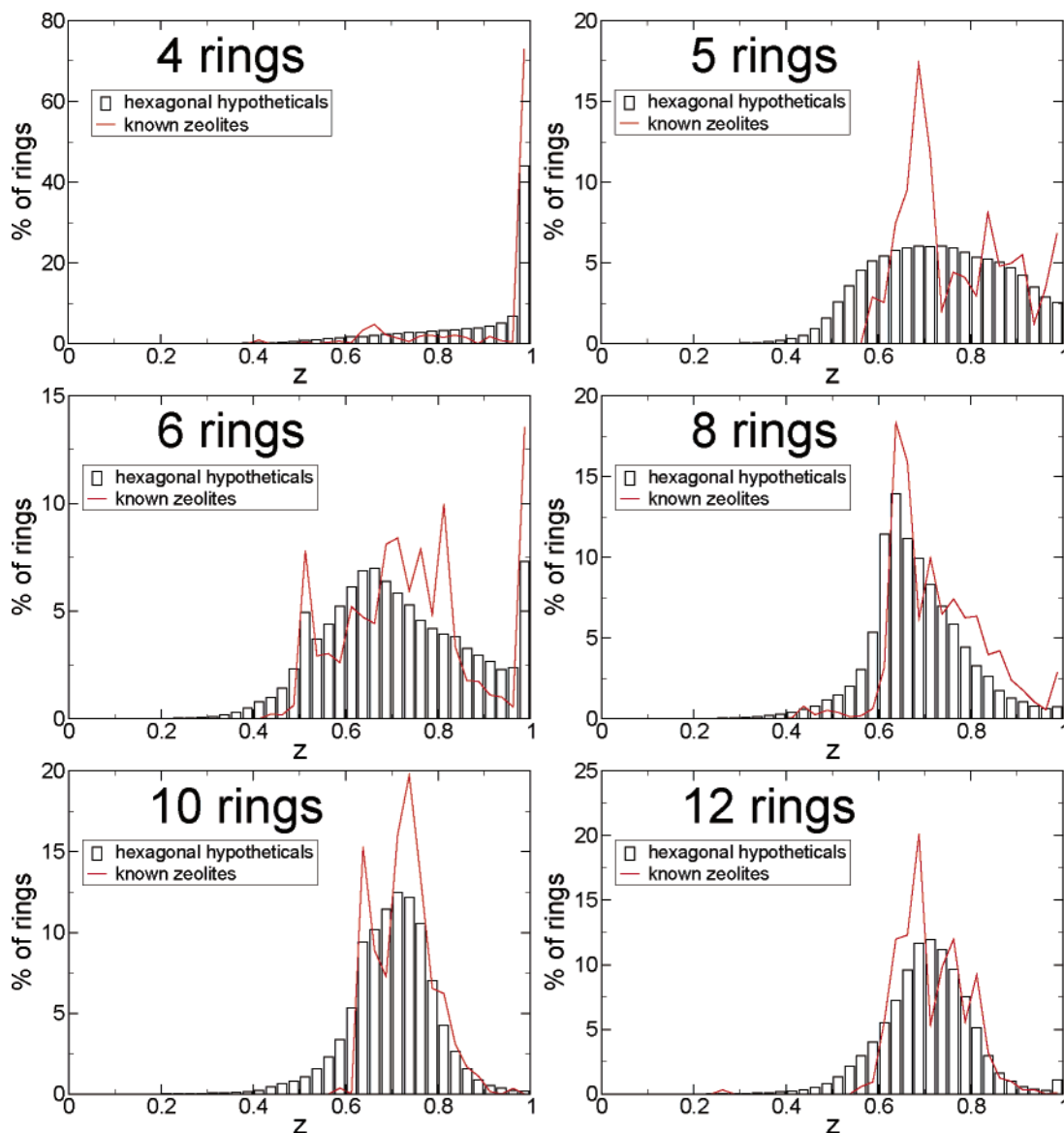


Figure 6. Ring flatness distributions for rings of 4, 5, 6, 8, 10, and 12 T atoms.

been found. As predicted from the hypotheticals in the earlier study, we now observe more 3, 9, and 16 rings in the known topologies.

In Figure 5, we have separated the contribution to the ring size distributions for low- and high-symmetry hexagonal space groups. Here, a space group is defined as low-symmetry if it contains 12 or fewer symmetry operations. High-symmetry space groups contain greater than 12 symmetry operations. The ring size distribution for structures found in high-symmetry space groups matches the known structures far better than does that for the low-symmetry structures. In both cases, though, the hypothetical topologies have more large rings than do the knowns. Low-symmetry topologies have far more odd numbered rings than both the known structures and the high-symmetry structures. Thus, we hypothesize that real hexagonal zeolites naturally tend to condense in the higher symmetry space groups.

In addition to ring size, one may also consider the flatness of the rings formed. We quantify ring flatness with the flatness parameter

$$z = 1 - \left(\frac{\lambda_3}{\lambda_1} \right)^{1/2} \quad (3)$$

where λ_3 and λ_1 are the smallest and the largest eigenvalues of the T atom distribution tensor, M , respectively.

$$M^{\alpha\beta} = \sum_{i=1}^N \delta r_i^\alpha \delta r_i^\beta \quad (4)$$

Here, $\delta r_i^\alpha = r_i^\alpha - N^{-1} \sum_{j=1}^N r_j^\alpha$ where r_i^α is the α -component of the position vector for atom i in the laboratory frame. The sum includes only the N T atom members of the ring, and it is independent of the identity of the T atoms. Diagonalization of M corresponds to changing the coordinate axis from the laboratory frame to the body frame. The eigenvalues of the diagonalized matrix are given by

$$\lambda_\alpha = \sum_{i=1}^N \overline{\delta r_i^\alpha}^2 \quad (5)$$

where the overbar denotes that the α -component of the position vector of atom i is with respect to the body axis. The subscript α also labels the eigenvalue, which we label in order of decreasing magnitude. Thus, λ_α is the mean square distance of the atoms in the ring in direction α of the body axis. The term

$(\lambda_3/\lambda_1)^{1/2}$ is approximately the ratio of the smallest width of the ring to the largest distance across the ring. For a planar ring, $\lambda_3 = 0$ and z is unity, because the mean square distance of the ring atoms in the direction normal to the plane is zero. In the limit of a spherical, crumpled ring, the distribution of ring atoms about each axis is the same, $\lambda_1 = \lambda_2 = \lambda_3$ and z is equal to zero. A fairly flat ring, such as the 18-membered ring in VFI (VPI-5), has a flatness of $z = 0.9$.

A comparison of flatness distributions for different ring sizes between the known zeolite topologies and the hypothetical hexagonal topologies from the database is shown in Figure 6 for a selection of ring sizes. The ring flatness distributions for known topologies are relatively rough and noisy due to the small sample size, whereas those from the database are quite smooth. One can still observe that the hypothetical flatness distributions match the known distributions well, with peaks and troughs in the distributions at approximately the same values of the flatness parameter. This increases our confidence that the hypothetical structures we are finding are rather zeolite-like.

4. Discussion

In the future, the database will be expanded to include structures from the triclinic, monoclinic, and the rest of the orthorhombic crystallographic space groups. As many of the known zeolite structures already occur in orthorhombic space groups, we expect to find many new topologies when sampling these additional space groups. At the current rate of finding structures per unit cell, we expect to eventually find approximately four million structures.

Upon completion of the database, the next step will be to refine the structures in the database. This process entails the addition of oxygens to the framework coordinates and energy minimization with a more detailed energy function²⁶ than that which zefsaII uses. Treacy and co-workers have shown that such refinement is possible using a force-field-based energy minimization method. For the enumerated structures produced by the Treacy and Foster enumeration search, roughly one-third of the topologies refine to good structures.²⁷ As our sampling-based approach produces structures that are explicitly energetically favorable, we expect a far higher fraction than one-third of our topologies to refine well. How many of these refined structures will then be thermodynamically accessible? Perhaps, 20% seems to be a conservative expectation, judging from a recent study by Simperler et al.²⁶

5. Conclusion

We have shown that the production of a database of hypothetical zeolite structures is feasible, and we have detailed a systematic method that we are using to generate structures for such a database. We expect that, by the end of our search for hypothetical structures, approximately four million new zeolite topologies will be found. We anticipate that many of these structures will be thermodynamically accessible. It is our long-term goal that structures from this database will be identified by their predicted material properties and become the subject of targeted synthesis studies by our experimental colleagues.

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