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Normal Mode Calculations of Faujasite-Type Zeolite Frameworks

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Normal mode calculations about the extended double six ring (D6R) subunit cluster model of Faujasite-type zeolites have been done by using the valence force field with reasonably adjusted force constants. We have studied for four *X, Y* zeolites species varying in M_f (Al/Si + Al) values. The calculated characteristic frequencies of D6R mode (ν_{D_6R}) and the rate of change of ν_{D_6R} with the mole fractions of aluminum, M_f(Al/Si + Al) values agree well with Flanigen's experimental data; the experimental slope is -79 cm^{-1}, while the calculated slope is -82 cm^{-1}. Those are the improved results as compared to Blackwell's theoretical study; his predicted slope is -94 cm^{-1}.

Introduction

Crystallographic techniques, such as X-ray diffraction or electron diffraction have been used for the determination of zeolite structures! But X-ray or electron diffraction techniques are not simple methods to determine the zeolite structure, because zeolites have the large unit cells and the many possible ways of tetrahedra linkage. What is worse is the uneasiness to make use of a large single crystal.

Therefore, a number of studies of zeolite frameworks have been made by infrared spectroscopy.[2-6] Especially the region of 200 to 1300 cm^{-1} in the infrared spectrum is very useful for zeolite structure analysis, because it contains the vibrations of the framework (Si, Al)O_4 tetrahedra.

Hence, Infrared spectroscopy and X-ray or electron diffraction techniques are complementary methods to each other for the determination of zeolite structure.

But the theoretical studies of zeolite frameworks have been done for limited cases because of the large size of zeolites unit cells. Recently, Blackwell studied the double-four-ring (D4R) in group 3 zeolites and the D6R in group 4 zeolites theoretically.[7-8] But in D6R case, the predicted spectrum was not compared well with experimental data.

In this study, the normal mode calculations were done for the extended D6R subunit cluster model ($Al_6Si_6O_{30}$), because the Faujasite-type zeolites, *e.g. X, Y,* are based on a D6R secondary building unit. We did the normal mode calculations for four *X, Y* zeolites species having different M_f(Al/Si + Al) values. Results were compared with Flanigen's experimental data and Blackwell's theoretical data.

Theory

The following modified potential is suitable for both intra and intermolecular motions.[9-11]

$$2V = K\sum_{ij}(\delta\gamma_{ij})^2 + H_\alpha\sum_{ijk}(\delta\alpha_{ijk})^2 + H_\tau\sum_{ijkl}(\delta\tau_{ijkl})^2 + \text{Interaction terms} \quad (1)$$

where K, H_α, and H_τ are stretching, bending and torsional force constant, respectively. The first term in eq.(1) represents the quadratic potentials between any two bonded atoms i and j. The next two terms describe the more commonly used angular deformation potentials; $\delta\alpha_{ijk}$ is the change in a angle between the bonds ij and jk, and $\delta\tau_{ijkl}$ is the change in a bond torsion. And the last interaction terms are the cross-terms describing the coupling between the above quadratic force fields, but these terms were not considered in this calculation.

The internal displacement coordinates $\delta\gamma_{ij}$, $\delta\alpha_{ijk}$, and *etc.* are

expanded with Cartesian displacement as follows

$$\left(\frac{\partial \gamma_{ij}}{\partial x_s}\right)_0 = \frac{(x_i - x_j)_s}{\gamma_{ij}^\circ} = \begin{cases} \Phi_{s,ij} & \text{for atom } i \\ -\Phi_{s,ij} & \text{for atom } j \end{cases} \quad (2)$$

$$\left(\frac{\partial \alpha_{ijk}}{\partial x_s}\right)_0 = \left(\frac{\alpha_{ijk}(x_s^\circ + \frac{1}{2}\Delta) - \alpha_{ijk}(x_s^\circ - \frac{1}{2}\Delta)}{\Delta}\right) = \Phi_{s,ijk} \quad (3)$$

The squares of the first derivatives constitute the force field matrix of the quadratic terms and the force field is represented as follows.

$$K\sum_{ij}(\delta\gamma_{ij})^2 = K\sum_{ij}\sum_{st} \pm \Phi_{s,ij}\,\Phi_{t,ij}\,\delta x_s\,\delta x_t \quad (4)$$

$$H_\alpha\sum_{ijk}(\delta\alpha_{ijk})^2 = H_\alpha\sum_{ijk}\sum_{st}\Phi_{s,ijk}\,\Phi_{t,ijk}\,\delta x_s\,\delta x_t \quad (5)$$

where s and t are the running index for Cartesian coordinates, x and Δ are the Cartesian axis and infinitesimal, respectively, and Φ_{ij} represents the element of directive cosine of the vector γ_{ij}.

The explicit explanations and derivations are given in Ref. 9 to 11.

Calculation and Discussion

There are a large number of normal modes, since the number of atoms in a unit cell of zeolites is very lage. But infrared spectra of zeolites are not resolved very well because of symmetry and group factor effects. Therefore, it is impossible to resolve and to observe all spectroscopically active modes. But each zeolite shows a characteristic infrared pattern. The spectra of zeolites with the same structural type and same structural group usually exhibit similarities.

The infrared spectra of zeolites can be grouped into two classes, so-called the internal vibrations of the TO_4 tetrahedra and the vibrations related to the linkages between tetrahedra. The ones usually are not sensitive to the frame-work structure. But the others are sensitive to the framework structure and to the existence of some secondary building unit and block polyhdera.

Flanigen *et al.*[5] did the experimental assignments of Zeolite's infrared spectra. We assigned the calculated normal modes referring to Flanigen's assignment.

The fact that typical modes of the double-ring external linkages do act like good group frequencies was approved by Blackwell's theoretical studies.[7,8] And so we accepted the Blackwell's postulate that there is a certain failry significant degree of uncoupling of the external double-ring from the large pore networks. We used the extended D6R subunit cluster model ($Al_6Si_6O_{30}$). The model to be studied is pictured in Figure 1. Olsen's structure of hydrated Na-X zeolite[12] was used for the geometry of model to be studied.

The geometry of the extended D6R subunit cluster model has $S_6(3)$ point group symmetry. This model ($Al_6Si_6O_{30}$) has 120 degrees of freedom of vibrational normal modes. When analyzed under point group S_6, the irreducible representations of the vibrational normal modes are $\tau_{vib} = 20A_u + 20E_u + 20A_g + 20E_g$. Infrared (IR) actives are the modes of types A_u and E_u and Raman actives are the modes of types A_g and E_g.

Cell dimensions of Faujasite-type zeolite, *X, Y,* change as the Si/Al ratio changes. Breck and Flanigen obtained the following equation by a least-squares linear fit to 37 data points of hydrous sodium *X, Y* systems with an experimental error of ± 0.005Å in a_0.[13]

$$a_0 = \frac{192}{1 + N_{Si}/N_{Al}}(0.00868) + 24.191 \quad (6)$$

where N_{Si} and N_{Al} are the number of silicon and aluminum per unit cell, respectively. Above equation also agreed well with Wright's data.[4] And so we used the above equation for the determination of cell dimensions as the Si/Al ratio changes.

In this study, we assumed that the model symmetry does not change as the Si/Al ratio changes and scaled all bonds evenly. Cell dimensions determined by eq (6) and evenly scaled bond-lengths are listed in Table 1.

When the Si/Al ratio changed, the masses were not changed from the alternate aluminum-silicon structure in order to investigate only the force constants' effects. Above approximation could be justified from the fact that a simple diatomic

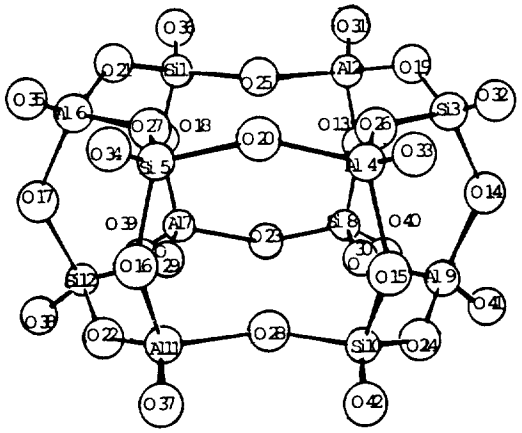

Figure 1. Extended D_6R subunit cluster model ($Al_6Si_6O_{30}$).

TABLE 1: Cell Dimensions[a] and Bond-Lengths[a] as M_f(Al/Si+Al) Changes

M_f(Al/Si+Al)	0.2621		0.2911		0.3690		0.4545	
a_0	24.628		24.676		24.806		24.949	
	T_1[b]	T_2[c]	T_1	T_2	T_1	T_2	T_1	T_2
T-01[d]	1.600	1.710	1.603	1.714	1.612	1.723	1.621	1.732
T-02[e]	1.596	1.692	1.599	1.695	1.608	1.704	1.617	1.714
T-03[f]	1.590	1.709	1.593	1.713	1.602	1.722	1.611	1.731
T-04[g]	1.586	1.695	1.589	1.699	1.598	1.708	1.607	1.718

[a] Dimensions is Å. [b] T_1 is Si. [c] T_2 is Al. [d] Oxyens of type O1 are 13, 14, 15, 16, 17, 18 in Figure 1. [e] Oxygens of type O2 are 19, 20, 21, 22, 23, 24 in Figure 1. [f] Oxygens of type O3 are 25, 26, 27, 28, 29, 30 in Figure 1. Oxygens of type O4 are 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, in Figure 1.

model had a change of 0.7% between the frequencies of a Si—O and an Al—O stretching mode if the force constants were identical.[7]

For the adjustment of stretching force constants with variation in bond length, we used the following optimized equation.

$$k = (-11.11)\,r + 22.35 \qquad (7)$$

where k is the stretching force constant and r is the bond length. The force constnts set used in this calculation as the Si/Al ratio changes is listed in Table 2. We assumed that bending and torsion force constants were the same as the Si/Al ratio changed, because the changes of bending and torsion force constants were so small that those could be neglected.

The calculated frequencies are listed in Table 3 to Table 6.

TABLE 2: Force Constants[a] Set Used in This Calculation as $M_f(\frac{Al}{Si+Al})$ Changes

$M_f(\frac{Al}{Si+Al})$	0.2621	0.2911	0.3690	0.4545
F_1 (Si-01 stretch)[b]	4.5722	4.5389	4.4389	4.3389
F_2 (Si-02 stretch)	4.6167	4.5833	4.4833	4.3833
F_3 (Si-03 stretch)	4.6833	4.6500	4.5500	4.4500
F_4 (Si-04 stretch)	4.7278	4.6944	4.5944	4.4944
F_5 (Al-01 stretch)	3.3500	3.3056	3.2056	3.1056
F_6 (Al-02 stretch)	3.5500	3.5167	3.4167	3.3056
F_7 (Al-03 stretch)	3.3611	3.3167	3.2167	3.1167
F_8 (Al-04 stretch)	3.5167	3.4722	3.3722	3.2611
F_9 (O-(Si or Al)-O bend)		0.3066		
F_{10} (Al-O-Si bend)		0.0462		
F_{11} (Torsion)		0.0317		

[a] Dimension is millidynes/Å. [b] The definition of oxygen types is the same as in Table 1.

TABLE 3: Calculated Frequencies[a] for IR Active Mode A_u as M_f(Al/Si+Al) Changes

$M_f(\frac{Al}{Si+Al})$	0.2621	0.2911	0.3690	0.4545
	1065	1060	1048	1035
	1032	1027	1015	1003
	1000	996	984	972
	874	870	860	849
	797	792	781	769
	703	700	692	683
	577[b]	575[b]	568[b]	561[b]
	500	498	493	487
	363	363	362	362
	334	334	334	334
	265	265	264	264
	232	232	232	232
	201	201	201	201
	198	198	198	198
	180	180	180	179
	139	138	138	138
	134	134	134	134
	116	116	116	116
	70	70	70	70
	69	69	69	69

[a] Dimension is cm^{-1}. [b] Double-six-ring mode frequencies (ν D_6R).

The our calculated frequencies of D6R mode (ν_{D_6R}) as the $M_f(\frac{Al}{Si+Al})$ changes are listed in Table 7 and compared with Flanigen's experimental data and Blackwell's predicted data. Plots, ν_{D_6R} *vs.* $M_f(\frac{Al}{Si+Al})$ are made in Figure 2. Our works

TABLE 4: Calculated Frequencies[a] for IR Active mode (E_u) as $M_f(\frac{Al}{Si+Al})$ Changes

$M_f(\frac{Al}{Si+Al})$	0.2621	0.2911	0.3690	0.4545
	1055	1051	1038	1025
	1048	1044	1031	1018
	994	990	978	966
	874	870	860	849
	791	786	776	764
	691	688	679	671
	623	621	613	606
	455	453	448	443
	352	352	352	351
	341	341	341	341
	308	308	308	307
	250	250	250	250
	213	213	212	212
	186	186	186	186
	152	152	152	152
	141	141	141	141
	123	123	123	122
	100	100	100	100
	71	71	71	71
	45	45	45	45

[a] Dimension is cm^{-1}.

TABLE 5: Calculated Frequencies[a] for Raman Active Mode (A_g) as $M_f(\frac{Al}{Si+Al})$ Changes

$M_f(\frac{Al}{Si+Al})$	0.2621	0.2911	0.3690	0.4545
	1067	1063	1050	1037
	1067	1063	1050	1037
	1045	1041	1028	1015
	983	979	968	957
	864	860	850	839
	764	760	750	739
	698	694	686	678
	691	688	680	671
	410	408	404	400
	351	351	351	351
	338	338	337	337
	285	285	285	285
	245	245	245	245
	214	214	214	214
	188	188	188	188
	182	182	182	182
	145	145	145	145
	142	141	141	141
	83	83	83	83
	77	77	76	76
	58	58	58	58

[a] Dimension is cm^{-1}.

TABLE 6: Calculated Frequencies[a] for Raman Active Mode (E_g) as $M_f(\frac{Al}{Si+Al})$ Changes

$M_f(\frac{Al}{Si+Al})$	0.2621	0.2911	0.3690	0.4545
	1058	1054	1041	1027
	1032	1028	1016	1004
	1007	1002	990	978
	1996	1992	889	867
	879	875	865	854
	800	795	784	772
	690	687	678	670
	555	553	547	541
	519	516	510	504
	359	359	359	359
	340	340	340	340
	299	299	299	299
	234	234	234	234
	220	220	219	219
	177	177	177	177
	166	166	166	166
	136	136	135	135
	129	129	129	129
	95	95	95	95
	69	69	69	69
	51	51	51	51

Dimension is cm^{-1}.

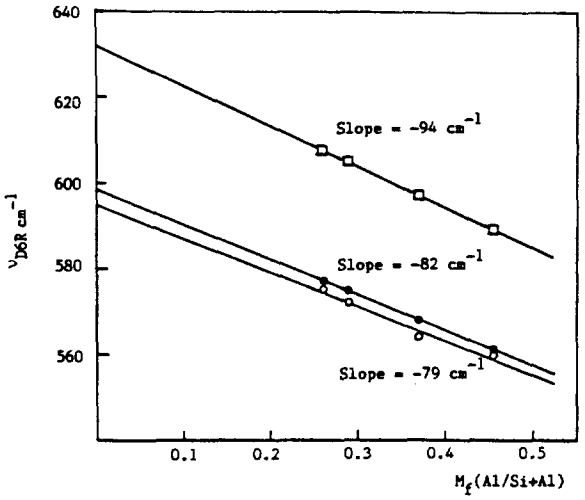

Figure 2. ν_{D_6R} dependence on M_f(Al/Si + Al) values. □ (Blackwell's predicted data); ● (our calculated data); o (Flanigen's experimental data).

TABLE 7: ν_{D_6R} of Faujasite-type Zeolite, *X*, *Y*

Zeolite	SiO_2/Al_2O_3	$M_f(\frac{Al}{Si+Al})$	ν_{D_6R}, cm^{-1} Flanigen's experimental data[a]	our calculated data	Blackwell's predicted data[b]
X	2.40	0.4545	560	561	586
Y	3.42	0.3690	564	568	594
Y	4.87	0.2911	572	575	602
Y	5.63	0.2621	575	577	604

[a] reference 5. [b] reference 8.

agree well with Flanigen's experimental data and are the improved results as compared with Blackwell's predicted data.

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