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Normal mode calculation and IR band assignments of A-type zeolite

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Normal mode calculation of A-type zeolite was carried out with the potential energy functions obtained from the constraint method. Mass-weighted cartesian coordinates and the pseudo-lattice method were used. The assignments of IR absorption bands were made with the calculated normal modes, by using the calculated absorption intensities of the modes and the degrees of contribution of the internal coordinates to the modes. The force constants of internal coordinate motions within the framework were also calculated and are compared with the empirical values.

Key words: Band assignments — Normal modes — IR-zeolites — Pseudo-lattice calculations — Force constants

1. Introduction

The normal mode calculation of a covalently bonding crystal with large unit cell contains many difficulties although several methods are available [1-5]. Recently, a calculation of the normal modes of zeolite was carried out in order to illuminate the vibrational motions of zeolite framework [6-8]. Since the vibrational spectra of zeolites are very widely used in investigating the physical and chemical properties of zeolites, the calculated vibrational modes may be useful in interpretating the zeolite behaviour. Various methods of calculating the normal modes, based on the Bloch theorem, are available [1-5], but we have adopted the pseudo-lattice method [7] proposed by No and Jhon, which can easily be applied to the zeolites [9-11]. We note that although the total potential energy of the zeolite system can be described by a set of force-field-type potential functions, this potential set can't predict the equilibrium geometry of the zeolite. The force constants used in the force-field potential were obtained from empirical rules [12, 13] or experimental data [14, 15]. Recently, a physically realistic potential energy function was obtained using the constraint method, and this has been used to investigate the static [16-19] and dynamic properties [20] of the zeolite framework.

In the assignment of IR absorption bands with the theoretically obtained normal modes, many criteria are needed because there are several candidates for each absorption band. These may be the vibration frequencies, selection rules for the infrared absorption, the characteristic spectrum of the rings, and the changes in the vibrational frequencies of the coupled modes with varying silicon-to-aluminium ratios [9]. It is also possible to calculate the absorption intensity of fundamental transition of each normal mode from the net atomic charges and the displacement vectors of the atoms in the model. Since the absorption bands have been characterized by experimentalists [21] in terms of internal coordinate motions such as T-O stretching and T-O-T or O-T-O bending, the classification of normal modes into the internal coordinate motions is necessary for a more accurate assignment of the bands. Therefore, in this study, the normal modes are projected onto an orthogonal internal coordinate set and are then classified into internal coordinate motions. The identification of the IR absorption bands will be made with these.

2. Calculation

2.1. Model ($Si_4Al_4O_{16}$)

For normal mode calculations on complicated molecules it is impossible to choose an orthogonal internal coordinate set which is symmetric with respect to all the symmetry elements of the model; mass-weighted cartesian coordinate system have therefore been used in this calculation [22-24]. This means that the internal coordinate set needed to describe the vibrational motion is different from that needed for the potential energy representation; consequently the additivity of the potential energy is assumed, and the internal coordinates used for the potential energy description contain many redundant coordinates. The $Si_4Al_4O_{16}$ double 4-ring (D4R) was used as a model, with the geometry taken from the x-ray crystallographic structure of dehydrated NaA-type zeolite [25]. This geometry, described in cartesian coordinates, is listed in Table 1. For the representation of an infinite framework with a finite model (D4R), the pseudo-lattice method was used in this calculation. Details of the application of the pseudo-lattice method to D4R is described in our previous papers [8, 9].

2.2. Potential energy functions

The potential energy functions suitable for the zeolite framework were obtained

Table 1. The geometry of the D4R model (in Å)

	X	Y	Z
Al	0.0	−2.2203	1.5433
Si	−2.2876	0.0	1.5963
O(1)	0.0	−2.7912	−0.0828
O(2)	0.0	−3.5829	2.5883
O(3)	−1.4402	−1.3209	1.9271

by the constraint method [16].

$$\sum_{i=1}^{k} \sum_{l=1}^{N} \sum_{j=1}^{3} \partial/\partial\alpha_i ABS(\partial V^0/\partial X_j^{0l}) = f \tag{1}$$

where $V^0 = V(\alpha_1, \alpha_2, \ldots\ldots\ldots, \alpha_k, x_1^{0l}, x_2^{0l}, \ldots, x_3^{0N})$, α_i is ith potential parameter, and x^l and x^{0l} represent the jth coordinate of lth atom when displaced and at equilibrium respectively. V is the stabilization energy of the crystal, which is expressed as

$$V = V_{\mathrm{el}} + V_{\mathrm{pol}} + V_{\mathrm{B}} + V_{\mathrm{NB}} + V_{\mathrm{bend}} + V_{\mathrm{tor}}. \tag{2}$$

The average net atomic charge of Na atoms, δ_{Na}, in A-type zeolite was obtained as 0.581 by No et al. [16]; net atomic charges of the atoms in the framework, δ_i, were calculated using Sanderson's electronegativity equalization conditions [26, 27] with Huheey's [28] atomic electronegativity set, a_i and b_i.

$$\sum_{i \neq \mathrm{Na}} \delta_i = -\delta_{\mathrm{Na}} \tag{3a}$$

$$a_i + b_i\delta_i = a_j + b_j\delta_j \tag{3b}$$

$$V_{\mathrm{el}} = \sum_{m} \sum_{n>m} \delta_m\delta_n / r_{mn} \tag{3c}$$

where r_{mn} represents the distance between the mth and nth atoms. For the good convergence of the electric fields, that is, the Madelung sums, the summation was carried out for all the $(\mathrm{SiAlO_2})\mathrm{Na}$ units within cubic crystal ($R = 2a_0$) [16–19].

$$V_{\mathrm{pol}} = -\tfrac{1}{2}\sum_{n} \sum_{j}^{x,y,z} \alpha_n \left[\left(\sum_{n \neq m} \vec{\varepsilon}_{mn}^{\,j}\right)^2\right] \tag{4}$$

where α_n is the atomic polarizability of the nth atom and $\vec{\varepsilon}_{mn}^{\,j}$ is the j-directional electric field at the position of atom n due to atom m.

$$V_B = \sum_{m} \sum_{n>m} De_{mn}\left(E^{-2\alpha_{mn}(r_{mn} - r_{mn}^{0'})} - e^{-\alpha_{mn}(r_{mn} - r_{mn}^{o'})}\right) \tag{5}$$

where De_{mn}, α_{mn}, and $r_{mn}^{0\prime}$ are the Morse potential parameters for atomic pair m, n. These atomic pairs are Si–O and Al–O bonds.

$$V_{\mathrm{NB}} = 4\varepsilon_{mn}[(\sigma_{mn}/r_{mn})^{12} - (\sigma_{mn}/r_{mn})^6] \tag{6}$$

where ε_{mn} and σ_{mn} are Lennard-Jones (6-12) potential parameters. This non-binding potential was used for O--O and O--Na pairs.

$$V_{\text{bend}} = \tfrac{1}{2}\sum_{n} (k'_n(\theta_n - \theta_n^0)^2 - k''_n(\theta_n - \theta_n^0)^3) \tag{7}$$

where k', k'', and θ^0 are bending potential parameters. The second term of the right side is introduced to describe the anharmonicity of angle bending motions. For the torsional potential function for the T-O-T-O coordinate, a harmonic potential was used:

$$V_{\text{tor}} = \sum_{m} k_{\text{tor}}(\phi_m - \phi_0)^2 \tag{8}$$

The potential parameters are summarized in Table 2.

The force constants are obtained in a cartesian coordinate system as

$$K_{ij}^{mn} = (\partial^2 V/\partial q_i^m q_j^n) = \sum_{l} (\partial^2 V_l/\partial q_i^m q_j^n) = \sum_{l} K_{ij}^{mn}(l) \tag{9}$$

where *mn* denote the atoms *m* and *n*, *i*, *j* denote cartesian coordinates, and *l* represents all the types of the potentials in *V*. Since the potential functions are described by internal coordinates, the calculation of force constants includes the coordinate transformations.

2.3. *Calculation of fundamental IR absorption intensities*

The absorption intensity was calculated from the dipole moment changes during vibration [29]. If the net atomic charges of the atoms in the model are assumed

Table 2. The refined potential parameters with $\delta_{\text{Na}} = 0.581$

Al-O, Si-O Bonding	$r^{0\prime}_{\text{Al-O}}$	1.770
	$r^{0\prime}_{\text{Si-O}}$	1.588
	$\alpha_{\text{Al-O}}$	1.368
	$\alpha_{\text{Si-O}}$	1.413
	$De_{\text{Al-O}}$	114.8
	$De_{\text{Si-O}}$	185.0
O-O, O-Na Non-bonding	$\sigma_{\text{O--O}}$	2.645
	$\sigma_{\text{O--Na}}$	2.477
	$\varepsilon_{\text{O--O}}$	0.227
	$\varepsilon_{\text{O--Na}}$	0.247
T-O-T, O-Al-O, O-Si-O Bending	$\theta^0_{\text{O-Al-O}}$	115.5
	$\theta^0_{\text{O-Si-O}}$	109.3
	$\theta^0_{\text{T-O-T}}$	141.5
	$k'_{\text{O-Al-O}}$	0.910
	$k'_{\text{O-Si-O}}$	0.432
	$k'_{\text{T-O-T}}$	0.076
	$k''_{\text{O-Al-O}}$	0.089
	$k''_{\text{O-Si-O}}$	0.043
	$k''_{\text{T-O-T}}$	0.009

k, k' in mdyne/Å, k'' in mdyne/Å^2, r^0 in Å, θ^0 in degrees, α in 1/Å, De in kcal/mol, ε in kcal/mol, σ in Å to be constant during each vibration, the relative intensities of the *i*th normal mode could be expressed as follows [8]:

$$I_i = 974.86\left[\sum_{k}^{x,y,z}\left(\sum_{j=i}^{N}\vec{D}_k(i,j)\right)^2\right] \tag{10}$$

where $\vec{D}_k(i,j)$ represents the dipole moment change due to the *j*th atom in the *k* direction of the *i*th normal mode. The dipole moment change matrix is

$$\boldsymbol{D} = \boldsymbol{R} \cdot \boldsymbol{\delta} \tag{11}$$

where $\boldsymbol{R}$ represents the normal coordinates described with respect to a cartesian basis set (not mass-weighted), and $\boldsymbol{\delta}$ is the diagonal matrix of the net atomic charges. Details are given in [8].

2.4. *Calculation of internal coordinate contributions to a normal mode*

A normal mode described by cartesian coordinate displacements, Q_i, can be transformed to the changes of an orthogonal internal coordinate set:

$$Q_i = \sum_j a_{ij} \cdot S_j \tag{12}$$

where $\{S_j\}$ is a set of internal coordinate displacement and the number of S_j being $3N-6$ or $3N$ depending on the method used. Each S_j can be expressed in terms of the $3N$ cartesian coordinates. The potential energy functions are described by the changes in internal coordinates, $\{q_l\}$, and generally $\{q_l\}$ doesn't form an orthogonal set; in our model many of the coordinates in $\{q_l\}$ are redundant. As a result, we use $\{q_l\}$ to describe the total potential energy, while vibrational motion is described by either $\{S_j\}$, or the cartesian coordinates $\{X_n\}$. The $\{q_l\}$ used to describe all contributions to equation 2 except for V_{el} are 32 stretching, 60 bending, 48 non-bonding, and 72 torsional coordinates. Since both the absorption bands and the empirically obtained force constants, k_j^s, are classified in terms of the coordinates $\{S_j\}$, the conversion of normal modes and force constants described by $\{X_n\}$ into those in terms of the $\{S_j\}$ coordinates may be useful. For the small displacements from the equilibrium position, the total potential energy expressed in Eq. (2) can be described in $\{q_l\}$ as

$$V = \sum_{l=1}^{m} V_l(q_l) + V_{\mathrm{ref}} \tag{13}$$

where V_l is the change in potential energy due to displacement of the *l*th internal coordinate, and *m* is the total number of internal coordinates in Eq. (1). Using the harmonic oscillator approximation, the total potential energy in cartesian coordinate system is:

$$2V = \sum_{n=1}^{3N} k_n^x X_n^2 + 2V_{\mathrm{ref}} \tag{14}$$

while in terms of the normal coordinates it is

$$2V = \sum_i k_i^Q Q_i^2 + 2V_{\mathrm{ref}} \tag{15}$$

where V_{ref} is the potential energy of equilibrium geometry and corresponds to the minimum point in the potential energy surface, V^0, of the A-type zeolite. The total potential energy described by Eq. (15) can be expressed as

$$2V = \sum_i \sum_j a_{ij}^2 k_i^s S_j^2 + 2V_{\mathrm{ref}} \tag{16}$$

Since additivity is assumed in the total energy description, the potential energy contribution of the jth internal coordinate in S_j to the ith normal mode can be expressed as a sum of each potential contribution:

$$2V_{ij}(S_j) = \sum_l [(\partial q_l / \partial S_j) S_j]^2 k_l^q + 2V_{\mathrm{ref}} \tag{17}$$

Denoting the projection of S_j on q_l $(\partial q_l / \partial S_j)$by g_{jl}, this becomes

$$2V_{ij}(S_j) = \sum_l g_{jl}^2 S_j^2 k_l^q + 2V_{\mathrm{ref}} = k_j^s S_j^2 + 2V_{\mathrm{ref}} \tag{18}$$

so that

$$k_j^2 = \sum_l g_{jl}^2 k_l^q \tag{19}$$

and the total potential is

$$\begin{aligned} V &= \sum_i V_i + V_{\mathrm{ref}} = \tfrac{1}{2} \sum_i \sum_j a_{ij}^2 \sum_l g_{il} k_l^q S_i^2 + V_{\mathrm{ref}} \\ &= \tfrac{1}{2} \sum_i \sum_j a_{ij}^2 V_j(S_j) + V_{\mathrm{ref}} \end{aligned} \tag{20}$$

The distribution of potential energy to S_j in ith normal mode is thus $a_{ij}^2 V_j$.

The a_{ij} can be obtained by projecting the ith normal mode onto S_j,

$$\vec{S}_k \cdot \vec{Q}_i = \sum_j a_{ij} \vec{S}_j \cdot \vec{S}_k \tag{21}$$

which leads to n inhomogeneous linear equations for each normal mode; these may be solved by the Gauss elimination method. In this study, both a_{ij} and g_{jl} are obtained within the restrictions of the D4R pseudo-lattice model.

The number of vibrational degrees of freedom depends on the method used in normal mode calculations. It is $3N$ in the calculation based on the Bloch theorem and is $3N-6$ in the cluster model.

3. Results and discussion

In Table 3, the vibrational frequencies, symmetric species and absorption intensities obtained from normal mode calculations are listed and are compared with the experimentally obtained absorption bands. In the assignment of the absorption bands to calculated normal modes, several criteria were used. Although many criteria were used in the assignment, the results seem to be still qualitative and semi-empirical. Since the vibrational spectrum of zeolite is sensitive to the framework structure and silicon/aluminum ratio, the absorption bands can be characterized by a combination of the internal coordinate motions: this is because

Table 3. The vibrational frequencies, symmetric species and absorption intensities obtained from normal mode calculations are compared with the experimentally obtained absorption bands

Infrared spectra	Vibrational frequencies	Symmetry species	Absolute intensity
	1095	*B*2(IR, R)	1779
	1091	*A*1(R)	
1090(*w*)	1086	*E*(IR, R)	0.02
1028(*w*)	1028	*E*(IR, R)	1121
	1027	*A*1(R)	
	1000	*B*2(IR, R)	0.01
	991	*A*2	
	985	*B*1(R)	
955(*s*)	980	*E*(IR, R)	536
	903	*E*(IR, R)	773
	899	*B*2(IR, R)	129
	828	*B*1(R)	
	812	*A*1(R)	
	811	*A*2	
	797	*E*(IR, R)	39
	790	*B*2(IR, R)	4
	789	*A*1(R)	
740–750 (*vw*, *sh*)	759	*E*(IR, R)	209
	737	*B*2(IR, R)	0.0009
	732	*E*(IR, R)	17
	727	*B*(2)(IR, R)	225
	712	*A*1(R)	
	688	*E*(IR, R)	40
660(*w*)	680	*B*2(IR, R)	875
	650	*A*1(R)	
	641	*E*(IR, R)	719
	573	*B*1(R)	
	571	*A*2	
550(*ms*)	567	*B*2(IR, R)	540
	520	*E*(IR, R)	10
	476	*B*1(R)	
	475	*E*(IR,R)	9
464(*m*)	456	*B*2(IR, R)	77
	455	*A*1(R)	
	452	*A*2	
	445	*E*(IR, R)	146
378(*ms*)			
	360	*A*2	
	307	*B*1(R)	
	288	*E*(IR, R)	0.07
	258	*B*1(R)	
260(*w*)	258	*E*(IR, R)	44
	245	*B*2(IR, R)	7
	244	*A*2	
	229	*E*(IR, R)	3

Vibrational frequencies and intensities are in cm^{-1} and km/mol, respectively one model calculation, specified by a certain structure and Si/Al ratio, can be described by one set of internal coordinates or of force constants. Therefore, the expansion coefficients, a_{ij} (the projection of ith normal coordinate to jth internal coordinate), calculated from Eq. (21) are necessary for more reliable assignments.

The degree of contribution of the internal coordinates (A_{im}) is defined by

$$A_{im} = \sum_k a_{ik}^2 \Big/ \sum_j a_{ij}^2, \tag{22}$$

where $\sum_k$ is the sum over the same kinds of internal coordinates described by m. m represents one of the Si-O(1), Si-O(2), Si-O(3), Al-O(1), Al-O(2), Al-O(3), Si-O-Al, O-Al-O, O-Si-O, or Si-O-Al-O internal coordinates. Values for A_{im} are summarized in Table 4. For the normalization of the expansion, $\sum_j a_{ij}^2$ is introduced as the denominator; because the normal coordinates described with respect to cartesian coordinates can't be completely expanded by the orthogonal internal coordinate set, the denominators take values between 0.9 and 1.0.

The modes higher than 800 cm^{-1} may be classified as stretching modes, although angle bending and torsional contributions are not negligible. In this region, due to symmetric restrictions, the degrees of the contributions of the same kind of T-O bonds, for example Si-O(1) and Al-O(1), or Si-O(2) and Al-O(2), to each normal mode are similar. Therefore, the first two IR active modes are T-O(1), the next two modes are T-O(2), and the following two modes are T-O(3) stretching modes. Below 550 cm^{-1}, the stretching contributions to normal modes are relatively small. In this region, both the T-O-T and the T-O-T-O contributions are relatively large compared with the modes higher than 550 cm^{-1}. However, over the whole frequency region, the contributions of any internal coordinate does not vanish, since the force constants of all the internal coordinate motions in the framework are of the same order, between $2 \sim 7$ mydne/Å, as shown in Table 5. Hence the coupling of internal coordinates is inevitable.

In order to represent the potential energy with the orthogonal internal coordinates in Eq. (18) or (20), the internal coordinate force constants, k^s, are calculated from Eq. (19) and are listed in Table 5. Here, the force constants are quite different from those obtained using empirical rules [12, 13] or experimental data [14, 15]. Since the internal coordinate motions in the framework are restricted both by the potential of the coordinate itself and by those formed with the environment atoms, the force constant k^s is larger than k^q for the same internal coordinate. In the normal coordinates of free molecules, the couplings between different kinds of internal coordinates are generally relatively small; however in a crystal, as in the zeolite framework, the force constants for bending and torsional coordinates are very large compared with those of free molecules and are comparable to those of stretching coordinates, and hence lead to large couplings of the internal coordinates. As shown in Table 6, all the atomic motions, even including T-O-T bending, have large force constants in the framework. The force constants of O---O coordinates are also very large, between 2.8 to 4.4 mydne/Å, implying that the motions of oxygen atoms are restricted by the other neighbouring

Table 4. The contribution of internal coordinates $\sum_k \alpha_{kj}^2$, A_{im}

	Stretching						Bending		Torsion	
Frequency	Si-O(1)	Si-O(2)	Si-O(3)	Al-O(1)	Al-O(2)	Al-O(3)	T-O-T	O-Al-O	O-Si-O	T-O-T-O
1095($B2$)	0.33	0.06	0.03	0.17	0.05	0.02	0.03	0.10	0.05	0.18
1086(E)	0.30	0.09	0.04	0.18	0.00	0.02	0.04	0.11	0.08	0.24
1028(E)	0.01	0.24	0.11	0.00	0.20	0.04	0.02	0.05	0.12	0.24
1000($B2$)	0.04	0.20	0.12	0.03	0.16	0.03	0.02	0.03	0.12	0.25
980(E)	0.02	0.03	0.26	0.00	0.03	0.10	0.07	0.05	0.14	0.32
903(E)	0.00	0.02	0.08	0.07	0.04	0.25	0.02	0.17	0.04	0.33
899($B2$)	0.00	0.01	0.15	0.04	0.02	0.15	0.07	0.14	0.06	0.36
797(E)	0.03	0.00	0.07	0.06	0.00	0.06	0.07	0.10	0.03	0.59
790($B2$)	0.00	0.00	0.01	0.00	0.00	0.05	0.11	0.15	0.11	0.57
759(E)	0.02	0.00	0.11	0.00	0.00	0.05	0.09	0.11	0.04	0.58
737($B2$)	0.04	0.00	0.02	0.03	0.01	0.18	0.12	0.03	0.04	0.53
732(E)	0.00	0.00	0.01	0.02	0.00	0.08	0.15	0.19	0.03	0.53
727($B2$)	0.01	0.01	0.00	0.00	0.02	0.01	0.05	0.15	0.13	0.62
688(E)	0.03	0.00	0.04	0.04	0.00	0.10	0.12	0.10	0.11	0.48
680($B2$)	0.08	0.00	0.01	0.11	0.02	0.01	0.03	0.14	0.03	0.57
641(E)	0.00	0.01	0.10	0.00	0.03	0.17	0.04	0.13	0.21	0.32
567($B2$)	0.02	0.01	0.22	0.03	0.00	0.26	0.17	0.06	0.07	0.17
520(E)	0.01	0.01	0.05	0.01	0.01	0.06	0.14	0.08	0.04	0.61
475(E)	0.02	0.00	0.02	0.02	0.00	0.03	0.10	0.13	0.08	0.58
456($B2$)	0.07	0.01	0.03	0.08	0.02	0.07	0.24	0.02	0.02	0.44
445(E)	0.08	0.01	0.07	0.10	0.00	0.11	0.19	0.07	0.06	0.31
288(E)	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.11	0.05	0.73
258(E)	0.01	0.00	0.30	0.00	0.00	0.00	0.12	0.08	0.09	0.68
245($B2$)	0.00	0.01	0.01	0.00	0.01	0.01	0.17	0.08	0.04	0.67
229(E)	0.00	0.00	0.01	0.00	0.00	0.00	0.20	0.05	0.02	0.72
93(E)	0.02	0.02	0.04	0.04	0.04	0.08	0.06	0.02	0.05	0.65

Table 5. The internal coordinate force constants (in mdyne/Å)

Internal coordinate	k^2	k^1	Used in Blackwell's calculation	Empirically obtained in mullite
$k_{\text{Al-O(1)}}$	5.939	3.707	3.292[a]	
$k_{\text{Al-O(2)}}$	6.667	3.800	3.183[a]	4.75[b]
$k_{\text{Al-O(3)}}$	6.027	3.456	3.024[a]	
$k_{\text{Si-O(1)}}$	6.472	4.983	4.975[a]	
$k_{\text{Si-O(2)}}$	7.09	5.177	5.417[a]	5.2[b]
$k_{\text{Si-O(3)}}$	6.249	4.800	5.053[a]	
$k_{\text{Al-O(3)-Si}}$	1.564	−0.090		0.084[c]
$k_{\text{Al-O(1)-Si}}$	1.634	−0.080		
$k_{\text{O(3)-Al-O(3)}}$	3.571	0.670		0.825[b]
$k_{\text{O(3)-Al-O(2)}}$	3.478	2.083		0.836[b]
$k_{\text{O(3)-Al-O(1)}}$	3.613	1.150		0.833[b]
$k_{\text{O(2)-Al-O(1)}}$	3.483	1.123		0.845[b]
$k_{\text{O(3)-Si-O(3)}}$	2.504	0.051		0.389[b]
$k_{\text{O(3)-Si-O(2)}}$	2.434	0.731		0.393[b]
$k_{\text{O(3)-Si-O(1)}}$	2.539	2.821		0.391[b]
$k_{\text{O(2)-Si-O(1)}}$	2.430	2.692		0.395[b]
$k_{\text{T-O-T-O}}$	2.269	0.042[c]		0.042[c]
$k_{\text{O(1)---O(2)}}$	4.438	0.043		
$k_{\text{O(1)---O(3)}}$	2.834	0.024		
$k_{\text{O(2)---O(3)}}$	4.308	0.050		
$k_{\text{O(3)---O(3)}}$	2.770	0.024		

[a] Calculated from BLSF-BR, $k^{BB}_{\text{T-O}}$ [6]

[b] Obtained empirically from the IR spectra of Mullite, $k^{M}_{\text{O-T-O}}$ and $k^{M}_{\text{T-O-T}}$ [15]

[c] Obtained from [14]

non-bonding oxygen atoms. Since the force constants corresponding to T-O-T, O-Al-O, O-Si-O, and O-T-O-T motions do not differ much in magnitude, most of the normal vibrations lower than 800 cm^{-1} are combinational motions of these coordinates. Therefore, with few exceptions, the vibrational motion in this region can't be characterized by an internal coordinate motion. For this reason, the normal modes were classified into the characteristic and coupled modes in our previous paper. The stretching force constants of Al-O bonds, calculated with the potential energy function, $k^{q}_{\text{Al-O}}$, are larger than those obtained from BLSF-BR, BLSF field based on Badger's rule, $k^{BB}_{\text{Al-O}}$; however $k^{q}_{\text{Si-O}}$s are smaller than $k^{BB}_{\text{Si-O}}$s. Except for Al-O bonds the force constants obtained from potential energy functions do not so much deviate from those obtained from empirically or experimentally obtained force constants. Since the A-type zeolite framework is composed of alternating Al-O and Si-O bonds, and both Si and Al are tetrahedrally coordinated by oxygen atoms, the bond character of the Al-O bonds is quite different from that of alumina.

If the force constant set k^s is used, where $\{S\}$ forms an orthogonal coordinate

Table 6. Calculated and observed vibrational frequencies assignments

	Calculated with BLSF-BR force constant set			Calculated with the potential set in Table 2			Significantly contributing potential energy terms		a_{ij} of significantly contributing coordinates	
IR	Frequency[a]			Motions			Frequency[a]		Intensity	
1090(*w*)	1091	*E*	Asymmetric stretching	1086	*E*	0.02			Si-O(1)	0.48
							Bonding		Al-O(1)	0.50
1050(*w*)	1068	*B*2		1028	*E*	1121	Bending	I	Si-O(2)	0.41
							N.B.		Al-O(2)	0.37
995(*s*)	981	*E*	Asymmetric stretching	980	*E*	536			Si-O(3)	0.32
									Al-O(3)	0.26
					--------------	850				
740-750	733			759	*E*	209			O-Al-O	0.36
							Bonding		T-O-T-O	0.45
660(*w*)	679	*B*2	Symmetric stretching	680	*B*2	875	Bending	II	Al-O(1)	0.22
									T-O-T-O	0.31
550(*ms*)	589	*B*2	Double ring	567	*B*2	540	N.B.		Al-O(3)	0.23
					--------------	550				
464(*m*)	450	*B*2	Double ring	456	*B*2	77			T-O-T	0.35
							Bending		T-O-T-O	0.31
378(*ms*)	381	*E*	6-ring				Torsion	III		
260(*w*)	260	*B*2	Pore opening of D4R+6-ring	258	*E*	44	N.B.		T-O-T-O	0.54
									T-O-T	0.22

[a] Symmetric species. Vibrational frequencies are in cm^{-1} and intensities are in km/mole

set, then the coordinates used for the description of vibrational motion and those used for the total energy expression in Eqs. (12) and (18) or (20), are the same internal coordinate set. Among 212 q coordinates, 16 Al-O, 16 Si-O, 12 T-O-T, 48 O-T-O, 72 T-O-T-O, and 48 O---O internal coordinates, in the pseudo-lattice method, $3N-3$ (69 in our model) orthogonal internal coordinates can be selected. In the selection of $\{S\}$ from $\{q\}$, the symmetric restrictions of the model must be considered.

Using the $A_{im}s$, the IR absorption band were assigned to the internal coordinates, and the results are summarized in Table 6 together with the previous assignments.

The potential energy functions used in this study may be physically meaningful because the crystal structures can be obtained with these potential functions [16-19] and the calculated vibrational frequencies arising from them agree well with experimental data. The non-bonding potential parameters of O--O and O--Na are very important for the determination of the crystal structure and the dynamic properties, i.e. the diffusion [20] of Na ion in the framework and the vibrational motions of framework [8].

Conclusion

For the normal mode analysis, the force constants obtained from the potential energy function, k^q, must be converted to the k^x in Eq. (14) or to k^s in Eq. (16). Using the additivity of the potential energy function, the k^s's can be obtained from Eq. (19). The vibrational motions, $\{Q\}$, must be described by $\{S\}$ or $\{X\}$. The expansion of $\{Q\}$ in terms of $\{X\}$ can easily be converted into the expansion of $\{S\}$ using projection operators and solving linear equations. Since the empirical force constants were selected to ensure that the theoretical number of IR active frequencies calculated with the force constants was compatible with the observed spectrum, the force constant set could be either k^q or k^s. Hence, conversions between k^q and k^s, or k^q and k^x, or k^s and k^x may be useful.

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