

Intensities of the Vibrational Spectra of Siliceous Zeolites by Molecular Dynamics Calculations. I. Infrared Spectra

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Two models based on electrooptical parameters and one model using the fixed-charge approximation are tested for the calculation of the infrared intensities of the vibrational modes deduced from molecular dynamics calculations of four siliceous zeolites: sodalite, faujasite, zeolite A, and silicalite. The best results are obtained from the electrooptical model containing two parameters: the equilibrium bond dipole moment of the SiO bond and the derivative of this dipole moment with respect to the SiO bond length. The ratio of these two parameters, 0.93 Å, determined previously is a good compromise permitting a reproduction of the relative intensities throughout the whole frequency range. The bond-stretching high-frequency range greater than 1000 cm⁻¹ is dominated by the second parameter. The first parameter essentially controls the frequency range less than 700 cm⁻¹.

1. Introduction

Zeolites are aluminosilicates where connected SiO₄ and AlO₄ tetrahedra give rise to microporous structures containing cavities and channels of molecular dimension. This structure is the basis for many industrial applications of zeolites ranging from separation to heterogeneous catalysis. These applications led to a development of numerous fundamental studies tending to get a better insight into the microscopic dynamics of the process in the cavities.

The methods of vibrational spectroscopy (IR absorption, Raman diffusion, and inelastic neutron scattering) were used to characterize these compounds and the interaction of these frameworks with adsorbed molecules. Unfortunately, a complete interpretation of the spectra is impossible because the high number of atoms in the unit cell and the existing disorder yield complicated spectra, and a direct correlation between structure and vibrational data does not exist. Thus, in the past decade, several groups developed numerical approaches to get a more quantitative description of the spectra. The techniques used included normal-mode analysis (NMA) and molecular dynamics (MD), which permit a correlation between spectral patterns and atomic motions.^{1–4} Most of the work performed up to now was concentrated on the determination of the vibrational frequencies and the identification of the vibrating entities. In a first step it was necessary to develop potential functions able to reproduce the structural properties and the dynamical data. This was achieved in the recent years either by using empirical force fields derived from small model molecules⁵ or by parametrization of potential functions from quantum chemical ab initio calculations.^{6–11} Unfortunately, up to now only one dimension of the spectra, the frequency, was really considered; the second one, the intensity, was taken into account by minimal models

using fixed-point charges for the IR spectra and a bond polarizability approach for the Raman spectra. Recently, the interest in calculating the IR absorption bands has grown, particularly for amorphous silica for which several techniques have been tested.^{12,13}

This report concerns the use of models derived from small molecules and quantum-mechanical considerations¹⁴ to the calculation of the IR intensities of the vibrational motions determined by MD calculations of models of zeolites to improve the quality of the discussion of these spectra. Section 2 introduces the different models tested. After the MD calculations performed are presented in section 3, the results are discussed in part 4.

2. Models for the Calculations of the IR Intensity

In the following text, bold letters are used to represent vectors, whereas the corresponding current letters indicate the absolute value (bond length or distance); the index $k = 1, K$ indicates a bond, and $i = 1, N$ counts atoms.

For a system at thermodynamical equilibrium the linear response theory^{15,16} relates the spectrum of the natural fluctuations of the dipole moment to the spectrum corresponding to its response to an external oscillating field. Assuming an isotropic medium the classical infrared absorption cross-section $I(\omega)$ can be calculated from the dipole moment time history $\mathbf{M}(t)$ obtained in a MD calculation as

$$I(\omega) = (4\pi^2\omega^2/3k_BcnT) \left\langle \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \sum_{\alpha=x,y,z} \left| \int_0^\tau dt \cdot \exp(i\omega t) \mathbf{M}_\alpha(t) \right|^2 \right\rangle \quad (1)$$

where ω is the angular velocity, T is the temperature, n is the refractive index, and k_B is the Boltzmann's constant, respectively.¹⁵ Therefore the IR spectrum can be obtained by Fourier transformation of the ensemble averaged dipole moment time correlation function $\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle$. Berens and Wilson¹⁵ discussed the role of the quantum corrections necessary to compare

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a classically calculated spectrum with the experimental quantum real spectrum. It turns out that the rotational corrections are negligible and that the vibrational corrections mainly concern the frequency shift due to the mechanical anharmonicity, whereas the contour corrections are small compared with the inhomogeneous broadening appearing in the experimental spectra of such highly disordered systems. Because this work is mainly concerned with the intensity estimation, and because the frequency shifts can simply be corrected by adjustment of the potential parameters, we did not attempt to make the suggested quantum corrections. Therefore the remaining relevant question is to find a model allowing the description of the dipole moment from the history of the Cartesian coordinates gained in a MD run.

The dipole moment is a quantity that is usually relatively simple to evaluate. Quantum-chemical programs give a direct access with satisfactory precision, but unfortunately the size of the systems considered does not allow such an approach because the computing time would be unreasonable. Among the parametrized methods, the concept of electrooptical parameters was applied to polyethylene.^{17–19} In these works it was shown that these parameters assigned to the bonds of a chemical system could be transferred to chemically similar compounds (from small alkanes to polyethylene). We will use a similar approach to apply parameters previously derived for small silicates to large silicate systems.¹⁴

The dipole moment \mathbf{M} of the system is described as a sum of bond dipoles \mathbf{m}^k according to

$$\mathbf{M} = \sum_{k=1}^K \mathbf{m}^k = \sum_{k=1}^K m^k \mathbf{e}^k \quad (2)$$

where the sum runs over the K bonds of the system; \mathbf{e}^k represents a unit vector directed along the bond k . The estimation of the autocorrelation function $\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle$ necessitates the calculation of $\mathbf{M}(t)$ at each step. Differentiating eq 2 leads to

$$d\mathbf{M} = \sum_{k=1}^K m^k d\mathbf{e}^k + \sum_{k=1}^K dm^k \cdot \mathbf{e}^k = \sum_{k=1}^K [m^k \cdot d\mathbf{e}^k + (dm^k/dr^k) dr^k \mathbf{e}^k] \quad (3)$$

This equation contains two so-called electrooptical parameters m^k and dm^k/dr^k . The first one corresponds to the equilibrium bond dipole moment, which changes its orientation during the motion, whereas the second one is the variation of the bond dipole moment caused by the change of the bond length. We can define two models termed I and I+II taking into consideration in eq 3 either the first parameter alone or both parameters. The dipole moment can thus be derived from the history of the atomic positions in the system. In this derivation it was supposed that the variation of the bond dipole moment is only caused by variations of the length of the same bond. A more general derivation would include the variation of one bond dipole moment with respect to all internal coordinates of the system and replace dm^k/dr^k by a sum $\sum dm^k/dR^m$ over the M internal coordinates R^m (bonds and angles) in the second term. This would lead to a larger number of parameters, difficult to determine, but also to a finer analysis of the information about the electronic molecular structure contained in the vibrational intensities.

Alternatively, the autocorrelation function is often evaluated according to the definition of the dipole moment \mathbf{M} with the

TABLE 1: Structural Data of the Calculated Zeolites

	sodalite	Zeolite A	faujasite	silicalite
space group	<i>Im3m</i>	<i>Fm3c</i>	<i>Fd3m</i>	<i>Pnma</i>
atoms/cell	36	576	576	288
unit cells	$2 \times 2 \times 2$	1	1	$1 \times 1 \times 2$
ref	22	23	24	25
equilibrium parameters used in the potential				
SiO (Å)	1.587	1.610	1.610	1.59
OSiO (°)	109.5	109.5	109.5	109.5
SiOSi (°)	159.7	150.6	142	149

help of a fixed-charge model assigning a charge q_i to each atom i .

$$\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle = \left\langle \sum_{i=1}^N q_i \cdot \boldsymbol{\sigma}_i(0) \cdot \sum_{i=1}^N q_i \cdot \boldsymbol{\sigma}_i(t) \right\rangle \quad (4)$$

Thus it can be deduced as previously from the history of the Cartesian atomic coordinates vectpr $\boldsymbol{\sigma}_i$, assuming that the charges in the system do not change during the MD run. Because charges are already defined for the potentials used in the MD runs, they can be transferred without any change to the intensity calculation, so that no new parameter has to be defined to calculate the second dimension of the spectrum. Such a calculation with fixed charges as parameters will be called model III.

In calculations using periodic boundary conditions the variation of the coordinates can be subject to discontinuities caused by atoms leaving the MD box on one side and entering on the other side according to the periodic conditions. One possible way to avoid these discontinuities is to use distances between atoms instead of coordinates; another one is to use the fact that the velocity \mathbf{v} is continuous. A charge-weighted velocity autocorrelation function can then be calculated according to

$$\left\langle \sum_{i=1}^N q_i \mathbf{v}_i(0) \cdot \sum_{i=1}^N q_i \mathbf{v}_i(t) \right\rangle = \left\langle \sum_{i=1}^N q_i \frac{d\boldsymbol{\sigma}_i(0)}{dt} \cdot \sum_{i=1}^N q_i \frac{d\boldsymbol{\sigma}_i(t)}{dt} \right\rangle = \left\langle \frac{d\mathbf{M}(0)}{dt} \cdot \frac{d\mathbf{M}(t)}{dt} \right\rangle \quad (5)$$

which therefore corresponds to the autocorrelation function of the derivative of the dipole moment with respect to the time t . Using the properties of the Fourier transformation the infrared cross-section can be calculated as

$$I(\omega) = (4\pi^2/3k_B c n T) \left\langle \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \sum_{\alpha=x,y,z} \left| \int_0^\tau dt \exp(i\omega t) dM_\alpha(t)/dt \right|^2 \right\rangle \quad (6)$$

which differs from eq 1 only by a factor ω^2 arising from the transformation of $d\mathbf{M}/dt$ instead of \mathbf{M} . Therefore it is also possible to obtain the IR spectra from the history of the atomic velocities in the system. Boulard et al. already used this method in a work in which they obtained the IR spectra of glasses from the autocorrelation function of the electric flux.²⁰ Model III calculations in this paper were performed according to this procedure.

3. Structural Models and MD Parameters

The structural data used for the definition of the MD boxes for the four different zeolites were those reported previously²¹ and are recalled in Table 1. The box was defined as a multiple number of unit cells, so that it had a nearly cubic shape with a box side length of about 25 Å, thus eliminating for the

TABLE 2: Force Constants Defining the Potential for Silicates^{10a}

coordinates	force constant
R	5.38
α	0.78
β	0.12
R/R (tetrahedra)	0.19
R/R (SiOSi bridge)	0.25
α/α	-0.11
α/α'	-0.32
R/α	0.13
R/α'	-0.13

^a R , α , and β indicate SiO bonds, OSiO angles, and SiOSi angles, respectively. A prime indicates an interaction force constant in which the two coordinates have no common bond. Units are mdyn/Å, mdyn Å/rad², and mdyn/rad according to the force constant.

comparison of the spectra the influence of the size and form of the unit cell, and the number of atoms used in the simulation.

The force field derived from ab initio analysis of small silicate clusters was transferred directly from our previous work on silicates.¹⁰ This harmonic force field contains three diagonal terms and six cross-terms coupling the internal coordinates, which are all given in Table 2. It accurately reproduced the structural data and the vibrational frequencies of zeolites.¹⁰

All calculations were performed in the NVE ensemble. The equations of motions were integrated with the Verlet algorithm using time steps of 2 fs. During the first 20 000 time steps the velocities were rescaled to the reference temperature of 300 K and then the simulation was performed over 50 960 time steps. The coordinates and velocities of all atoms were stored every fifth step for the last 40 960 time steps (81.92 ps). During the analysis of the results in a preliminary phase it turned out that the relative intensities significantly depend on the initial conditions even after increasing the duration of the equilibration step. This indicates that the statistical assignment of atomic velocities from a Maxwell distribution does not necessarily lead to a proper distribution of the vibrational energy over the normal modes ($k_B T$ per normal mode) after equilibration. The equilibration steps really perform the equipartition of potential and kinetic energy of the system, but because of the harmonic approximation used for the potential, the energy exchange between the vibrational modes is not fast enough to achieve the proper distribution. To correct this artifact the spectra were calculated as mean value of 10 independent MD runs performed with different starting conditions. (For each independent run the spectra were averaged over 7169 time origins.) Several tests have shown that the error in reproducibility of the calculated intensities under such conditions is smaller than 10%, a value compatible with the experimental precision. The theoretical calculated frequency step in one spectrum is 3.26 cm⁻¹.

Finally we transferred the electrooptical parameters determined previously for small clusters¹⁴ to the periodic zeolitic systems. Using the experimental relative infrared intensities of SiH₄ and H₈Si₈O₁₂, the normal modes calculated in ref 5 and the electrooptical formalism presented in refs 17–19 and summarized in the preceding section of this article, it was possible to derive one parameter permitting the estimation of the infrared intensity of large siliceous systems. Assuming that most of the bond dipole variation arises from the variation of the bond length, it is possible to only consider the parameters μ_0^{SiH} , μ_0^{SiO} , $d\mu^{\text{SiH}}/dR^{\text{SiH}}$, and $d\mu^{\text{SiO}}/dR^{\text{SiO}}$. For the determination of these four parameters three infrared bands were available in the spectra of the two molecules: two stretching modes of the SiH bonds in both molecules and one stretching mode of the SiO bonds. Because we are mostly interested in

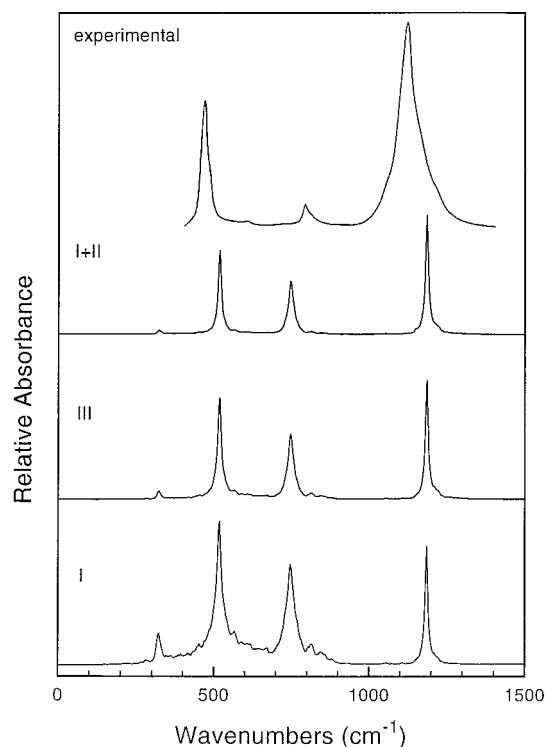


Figure 1. Experimental^{127,28} and calculated infrared spectra of siliceous sodalite. (See the definition of the models in the text.)

relative intensities, the two parameters of the SiO bonds can be reduced to only one, which can be the ratio of the equilibrium bond dipole moment to its derivative with respect to the bond length. The value 0.93 Å of this ratio led to the best calculated relative intensities for the two considered molecules. This value compares satisfactorily with the MNDO evaluation of the same ratio (1.23 Å) determined by Davidova et al.²⁶ for the molecule Si₇O₉(OH)₃(C₅H₉)₇, in particular, if one considers that in this molecule SiC and Si–OH bonds modify the electronic distribution around the silicon atoms and that these authors included all electrooptical parameters between coordinates with common atoms. Because our zeolitic systems only contain SiO bonds, the value 0.93 Å derived from experimental relative intensities was applied in the following intensity calculations. For model III the atomic charges were set to 1.6 and -0.8 electronic charges for the silicon and oxygen atoms, respectively.²¹

4. Results and Discussion

The spectra calculated with the different models for the zeolites are compared with experimental spectra from the literature in Figures 1–4. The corresponding calculated frequencies are gathered in Tables 3–6. The overall agreement concerning the frequencies is very satisfactory as could be expected from previous studies using the same force field.^{10,11} A more precise analysis is difficult because the experimental samples were never purely siliceous and the Si–Al substitution led to specific bands or shoulders.⁴ Obviously the high-frequency group between 1100 and 1200 cm⁻¹ is calculated at too high a frequency. This is particularly evident for sodalite in which only one band exists, but also for the other zeolites in which more complex structures render the comparison more difficult. The relative mean deviation of the vibrational frequencies for the four zeolites is about 5%.

The analysis of the results concerning the intensities is difficult because the reference experimental spectra from the

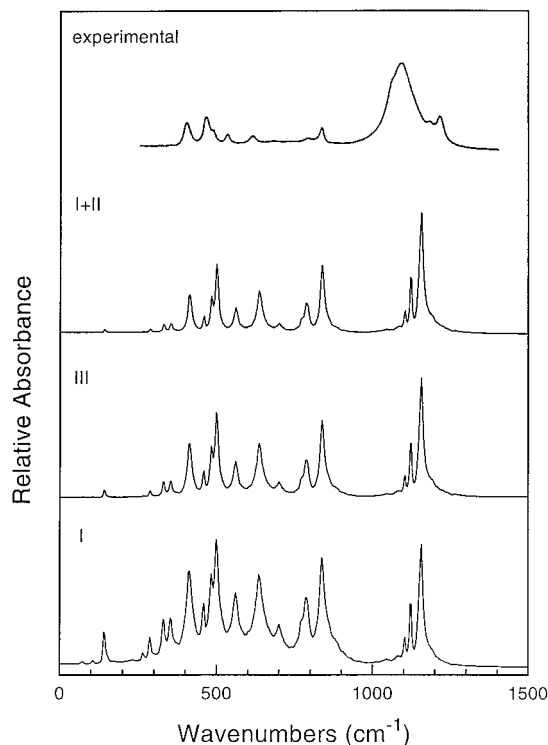


Figure 2. Experimental²⁹ and calculated infrared spectra of siliceous faujasite. (See the definition of the models in the text.)

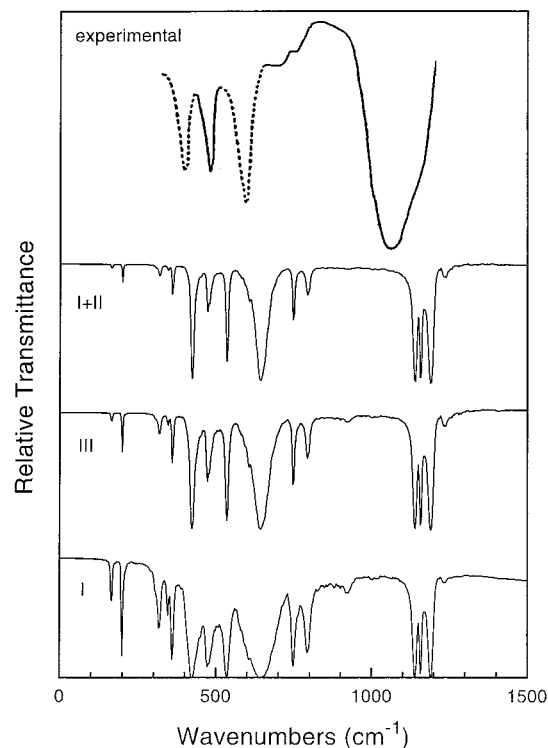


Figure 3. Experimental³⁰ and calculated infrared spectra of siliceous zeolite A. (See the definition of the models in the text.) According to the original ref 30, the solid line represents vibrations inside the SiO₄ tetrahedra, whereas the broken line corresponds to external motions of the tetrahedra.

literature were obtained from aluminated samples for which the dehydration process was not always complete but difficult to estimate from the reports. Therefore the discussion can only be qualitative. In Tables 3–6 the assignment of the calculated bands to the experimental ones was performed by taking into account

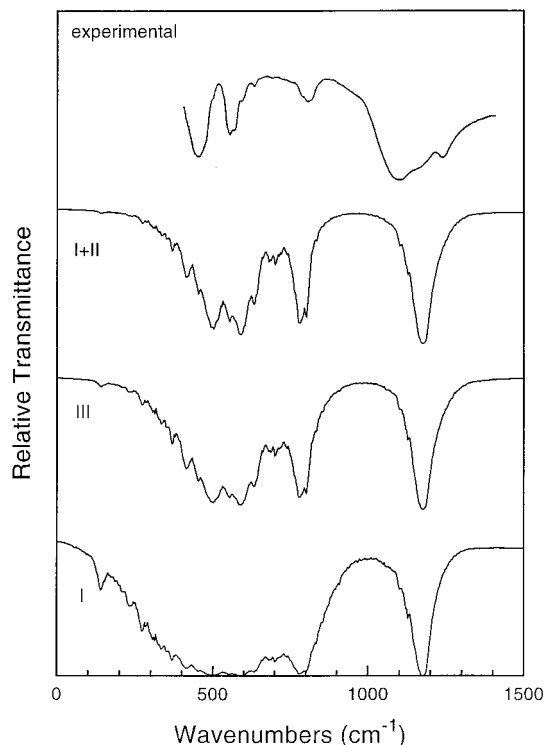


Figure 4. Experimental³¹ and calculated infrared spectra of siliceous silicalite. (See the definition of the models in the text.)

TABLE 3: Comparison of the Experimental and Calculated Spectra of Siliceous Sodalite

calculation	experiment	ref
1186 s	1109 vs	27
746 m	788 w	27
518 m	460 m	27
322 vw	289 –	28

vs, s, m, w, and vw mean very strong, strong, medium, weak, and very weak, respectively.

TABLE 4: Comparison of the Experimental and Calculated Spectra of Siliceous Faujasite

calculation	experiment ²⁹
1156 s } 1121 m } 1104 w }	1085 vs
837 m	833 m
785 w	789 w
700 vw	681 vw
635 m	610 w
560 w	529 w
498 m } 482 w } 459 w }	460 m
414 m	400 m
352 vw	350 vw
329 vw	319 vw
287 vw	291 vw
140 vw	–

vs, s, m, w, and vw mean very strong, strong, medium, weak, and very weak, respectively.

not only the frequencies, but also the intensities, particularly trying to avoid bands calculated with a significant intensity that could have no counterpart in the experimental spectrum.

Obviously for all zeolites the calculated bands always have too narrow a width. This can be expected from the two approximations used. First, the calculation contains essentially harmonic terms; therefore, the energy exchange between the

TABLE 5: Comparison of the Experimental and Calculated Spectra of Siliceous Zeolite A

calculation	experiment ³⁰
1238 vw	
1189 s	
1156 m	1151 vw
1140 m	1044 vs
792 w	750 vw
746 w	698 vw
642 s	581 s
534 m	475 m
472 w	—
423 m	393 m
358 w	—
345 vw	—
316 vw	—
199 w	—
166 vw	—

vs, s, m, w, and vw mean very strong, strong, medium, weak, and very weak, respectively.

TABLE 6: Comparison of the Experimental and Calculated Spectra of Siliceous Silicalite

calculation	experiment ³¹
1176 s	1096 vs
782 m	804 w
700 vw	688 vw
632 w	628 w
590 m	552 m
554 w	~492 vw
502 m	444 s
453 vw	—
414 w	—
368 vw	—

vs, s, m, w, and vw mean very strong, strong, medium, weak, and very weak, respectively.

normal modes arising from mode coupling is greatly reduced and the lifetime of the states is increased correspondingly. Second, the experimental spectra contain inhomogeneous broadening which is absent from the model assuming a perfect crystal. With consideration of these remarks the agreement between the calculated spectra and the experimental data is satisfactory for all models. A direct comparison of the three models is not straightforward because the Cartesian and internal coordinate systems and the parameters (charges and bond dipole moments) are not simply related. A close comparison of all figures indicates a high similarity between models I + II and III noticed previously for the small clusters.¹⁴ We will analyze the spectra considering first the SiO stretching modes over 700 cm⁻¹, then the deformation modes between 400 and 700 cm⁻¹, and finally the low-frequency range under 500 cm⁻¹.

The analysis of the IR active stretching bands of several triatomic bent T—O—T systems (e.g., water, sulfur dioxide, phosgene or methylene group in polyethylene) shows that usually the asymmetric stretch motion is only slightly more active than the symmetric one. On the contrary, in zeolites the asymmetric motion at high frequencies around 1100 cm⁻¹ is by far more active than the symmetric motion identified around 800 cm⁻¹. In their study of polyethylene Abbate et al.¹⁸ clearly indicate that most of the intensity is arises from the term dm/dr , all other parameters and particularly the equilibrium dipole moment bringing only small corrections. Because of the presence of three-dimensional cyclic structures in zeolites it is no longer possible to stretch bonds without changing the orientation of neighboring ones. Model I, which contains only the equilibrium dipole moment as a parameter, yields in the high-frequency range the intensity arising from the connectivity

through reorientation of bond dipole moments. As expected the corresponding intensity is too low with respect to the spectrum at lower frequency. The addition of the derivative dm^k/dr^k term in model I+II improves this result and leads to calculated data in better agreement with the measured values over 700 cm⁻¹. At present the agreement is not completely satisfactory because a higher relative intensity is expected above 1000 cm⁻¹. This deficiency can be overcome by the introduction of electrooptical parameters such as dm^{k1}/dr^{k2} (variation of the bond dipole moment k_1 with the stretch of a neighbor bond k_2) or $dm^k/d\alpha$ (variation of the bond dipole moment with respect to an angle internal coordinate) as shown by trials to introduce such terms into the intensity model in the report on the intensities of the IR spectra of small molecules.¹⁴ Because the number of experimental data is not sufficient to determine these parameters we were not able to further improve this part of the spectrum. Finally, the fixed-charge model III yields spectra similar to those of model I+II in the high-frequency region. The variation of the dipole moment can be written in the system of Cartesian coordinates as:

$$d\mathbf{M} = \sum_{i=1}^N [q_i d\sigma_i \mathbf{e}_i + q_i \sigma_i d\mathbf{e}_i + dq_i \sigma_i \mathbf{e}_i] \quad (7)$$

where q_i represents the atomic charges, and σ_i and \mathbf{e}_i represent the distance between atom i and the origin and a unit vector along this distance with respect to the Cartesian frame of the system studied, respectively. The index i runs over all atoms of the system. The third term is not accounted for in model III. The first term leads to a variation of the dipole moment through the variation of distances of the atoms to the origin, whereas the second term is suitable to represent variations of the orientation of the dipole moment. Thus model III potentially has the flexibility to represent the same types of variations as model I+II at least as long as relative intensities are concerned.

The central part of the spectrum between 400 and 700 cm⁻¹ is generated by motions mostly involving variations of the OSiO angles. In this region the agreement with the experimental relative intensities is very satisfactory and the similarity of the relative intensities of the different models is very high. This renders a more detailed discussion rather difficult, but it indicates that compensation effects of the different parameters occur in this spectral region and that the parameters defined in this study correspond to a good balance for a simulation of the relative intensities. A criterion to decide between the models cannot be expected from this spectral region, but the fact that model I yields quite satisfactory relative intensities indicates that in this frequency range the changes of bond orientations caused by angle bendings are responsible for most of the intensity.

The comparison with experimental data is difficult in the region of very low frequencies because the number of available measured spectra is reduced between 200 and 400 cm⁻¹. Under 200 cm⁻¹ the existing experimental spectra are difficult to use because aluminated samples were measured and these spectra also contained absorption bands involving the degrees of freedom of the charge-balancing cations. In a complete study performed on EMT zeolite with different charge-compensating cations (Li, Na, K, Rb, Cs) Li yields spectra very similar to siliceous samples, because the low weight and small ionicity of the ion lead to lower signals at higher frequencies than the other cations. This indicates that under 400 cm⁻¹ the framework modes, which are mostly driven by bending motions of the SiOSi angles, only show a very low intensity (Figure 3 of ref 32).

Nevertheless, the comparison of the calculated spectra permits some conclusions about the processes causing the observed absorption bands in this region. Models III and I + II produce similar spectra at low frequencies. In the dipole moment variation of eq 7, the two first terms correspond to model III, which qualitatively reproduces the experimental intensity in the low-frequency region. Thus, the third term, which contains the variation of the charges during the motions, cannot be responsible for a significant participation to the experimental intensity. The comparison of models I and I+II indicates that the relative intensity of the low-frequency range decreases when term II is added in the calculation. At very low frequencies, where large amplitude motions of larger parts of the unit cell can be expected, strong local dipole moments can occur, the combination of which can explain the observed IR bands. The intensity of the bands is too high in model I; in Figures 2 and 3 these intensities are significant, although only weak bands appear in the experimental spectra, even in aluminated zeolites where the presence of cations gives rise to stronger bands.³² It is therefore possible to conclude that the model I+II contains a good compromise of parameters for changes in orientations and for charge fluxes and may therefore be considered as the best of the three possibilities explored in this paper.

5. Conclusions

The results obtained during this study of siliceous zeolites show that the parameters deduced from a work on the vibrational infrared intensities of small silicate clusters¹⁴ are transferable to larger systems. The numerical value of the ratio of the equilibrium bond dipole moment to its derivative with respect to the bond length was 0.93 Å. This leads to intensities in very good agreement with the available experimental data. Some discrepancies in the high-frequency range indicate that the parameter set could be extended by supplementary parameters. But their definition necessitates the complete analysis of new sets of silicate clusters and the improvement of this approach with quantum mechanical model calculations permitting the definition of the most significant supplementary parameters and of their signs and order of magnitude. Considering their quality, the present set of parameters is sufficient, for the qualitative interpretation of the experimental spectra. The comparison of the three different models also indicates that a reliable simulation of the spectra necessitates a model with flexibility sufficient to take into account the orientation of the bonds and the charge fluxes inside the bonds during the motions. In the present form this approach permits a good analysis of systems as different as zeolites built from sodalite blocks or silicalite with very different IR spectra and thus can be expected to be more widely transferable to other silicate classes. Finally it is possible to state that in the high-frequency range over 1000 cm⁻¹ the $dm^k/d\tau^k$ parameter plays the most important role, whereas the equilibrium dipole moment drives the lower frequency part of the spectrum under 700 cm⁻¹.

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