

Ab Initio and Classical Simulations of the Temperature Dependence of Zeolite Pore Sizes

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Supplemental Information

This file contains the following information:

- 1 System size of zeolites and cpu time per dynamics step by Ab-initio simulation .
- 2 Detail information of force fields parameters.
- 3 Infrared spectrum for SOD and FER.

Table S1: simulation system size and CPU time per molecular dynamic step in CPMD

Zeolite type	SOD	FER	Silicalite
Number of Valence electrons	196	588	1568
CPU time(s)	8.6	256	3900

Potential forms and parameters

$$V_{\text{buckingham}}^{\text{short}} = A \exp\left(\frac{-r}{\rho}\right) - \frac{C}{r^6} \quad (\text{S1})$$

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$$V_{\text{morse}}^{\text{short}} = E\{[1 - \text{EXP}(-k(r - r_0))]^2 - 1\} \quad (\text{S2})$$

$$V_{\text{harmonic}}^{\text{tbp}} = \frac{K}{2}(\theta - \theta_0)^2 \exp\left(-\frac{r_{ij}^8 + r_{jk}^8}{\rho^8}\right) \quad (\text{S3})$$

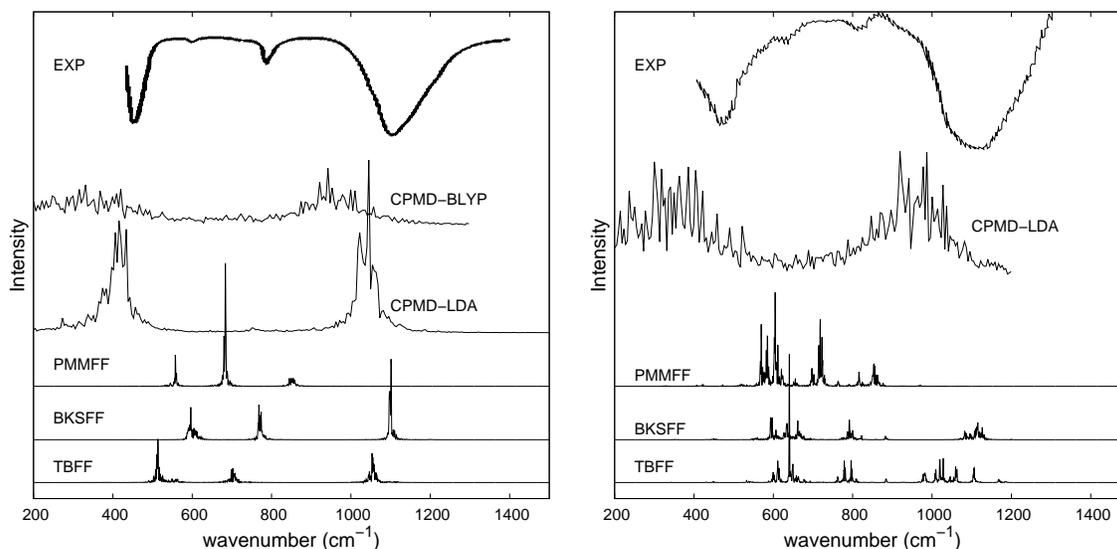


Figure S1: IR spectrum for SOD (left) and FER (right) at 300K

Experimental spectra in Figure S1 were obtained from Deman^{S5} and Zheng.^{S6} In CPMD calculations, it is traditionally thought that the BLYP functional improves the accuracy as compared to the LDA functional. However, previous work determining the vibrations in Furan and Thiophene by Elazhary^{S7} has demonstrated that BLYP is not necessarily better than LDA. Both BLYP and LDA functionals were used in our IR calculations for SOD to evaluate the effectiveness of different functionals. According to figure S1, Although The LDA functional shows higher accuracy than BLYP in calculating the characteristic peak positions, it still consistently underestimates vibrational frequencies for both SOD and FER by 10%. The relationship between the frequency ω and the vibrational amplitude for a single harmonic oscillator is given by:

$$K_P = \frac{1}{2}m\omega^2x^2 \quad (\text{S4})$$

Table S2: Force field Parameters

	TBFF ^{S1}	YOKFF (fit from Yamahara ^{S2})
charge		
Si	2.4	2.4
O	-1.2	-1.2
	Buckingham	Morse
$A_{\text{Si-O}}(\text{ev})$	17796.1	$E_{\text{Si-O}}(\text{ev})$ 2.15486
$\rho_{\text{Si-O}}(\text{\AA})$	0.2049	$k_{\text{Si-O}}(\text{\AA}^2)$ 1.75456
$C_{\text{Si-O}}(\text{ev \AA}^6)$	135.4	$r_{\text{Si-O}}(\text{\AA})$ 2.0
$A_{\text{O-O}}(\text{ev})$	1305.9	Buckingham
$\rho_{\text{O-O}}(\text{\AA})$	0.3594	$A_{\text{O-O}}(\text{ev})$ 4266.3079
$C_{\text{O-O}}(\text{ev \AA}^6)$	196.1	$\rho_{\text{O-O}}(\text{\AA})$ 0.3
		$C_{\text{O-O}}(\text{ev \AA}^6)$ 4.14764
	Three body for O-Si-O	$A_{\text{Si-Si}}(\text{ev})$ 99.7871
$K(\text{ev rad}^2)$	700.96	$\rho_{\text{Si-Si}}(\text{\AA})$ 0.2
$\rho_1(\text{\AA})$	0.3277	$C_{\text{Si-Si}}(\text{ev \AA}^6)$ 0
$\rho_2(\text{\AA})$	0.3277	
$\theta_0(\text{rad})$	109.53	
	BKSFF ^{S3}	PMMFF ^{S4}
charge		
Si	2.4	2.4
O	-1.2	-1.2
	Buckingham	Morse
$A_{\text{Si-O}}(\text{ev})$	18003.7572	$E_{\text{Si-O}}(\text{ev})$ 0.240554
$\rho_{\text{Si-O}}(\text{\AA})$	0.205205	$k_{\text{Si-O}}(\text{\AA}^2)$ 2.006700
$C_{\text{Si-O}}(\text{ev \AA}^6)$	133.5381	$r_{\text{Si-O}}(\text{\AA})$ 2.100000
$A_{\text{O-O}}(\text{ev})$	1388.7730	$E_{\text{O-O}}(\text{ev})$ 0.042395
$\rho_{\text{O-O}}(\text{\AA})$	0.362319	$k_{\text{O-O}}(\text{\AA}^2)$ 1.379316
$C_{\text{O-O}}(\text{ev \AA}^6)$	175.0000	$r_{\text{O-O}}(\text{\AA})$ 3.618701
	MBKSFF	
charge		
Si	2.6	
O	-1.3	
	Buckingham	
$A_{\text{Si-O}}(\text{ev})$	18003.7572	
$\rho_{\text{Si-O}}(\text{\AA})$	0.205205	
$C_{\text{Si-O}}(\text{ev \AA}^6)$	133.5381	
$A_{\text{O-O}}(\text{ev})$	1388.7730	
$\rho_{\text{O-O}}(\text{\AA})$	0.362319	
$C_{\text{O-O}}(\text{ev \AA}^6)$	175.0000	

Underestimating the vibrational frequency results in an overestimation in the vibrational amplitude. As such a correction of 10% must be accounted for in the computations of σ by CPMD. The peak between 1000 cm^{-1} and 1100 cm^{-1} was assigned to the asymmetrical stretch.^{S8} The peaks at $1000\text{--}1100\text{ cm}^{-1}$ and 800 cm^{-1} are reproduced with high accuracy using BKSFF. However, TBFF shows higher accuracy in calculating the peaks near 400 cm^{-1} . PMMFF always underestimates the frequencies in the high frequency region and overestimates those in the lower region.

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