

# Normal Mode Analysis in Zeolites: Toward an Efficient Calculation of Adsorption Entropies

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 Supporting Information

**ABSTRACT:** An efficient procedure for normal-mode analysis of extended systems, such as zeolites, is developed and illustrated for the physisorption and chemisorption of *n*-octane and isobutene in H-ZSM-22 and H-FAU using periodic DFT calculations employing the Vienna Ab Initio Simulation Package. Physisorption and chemisorption entropies resulting from partial Hessian vibrational analysis (PHVA) differ at most  $10 \text{ J mol}^{-1} \text{ K}^{-1}$  from those resulting from full Hessian vibrational analysis, even for PHVA schemes in which only a very limited number of atoms are considered free. To acquire a well-conditioned Hessian, much tighter optimization criteria than commonly used for electronic energy calculations in zeolites are required, i.e., at least an energy cutoff of 400 eV, maximum force of  $0.02 \text{ eV/\AA}$ , and self-consistent field loop convergence criteria of  $10^{-8} \text{ eV}$ . For loosely bonded complexes the mobile adsorbate method is applied, in which frequency contributions originating from translational or rotational motions of the adsorbate are removed from the total partition function and replaced by free translational and/or rotational contributions. The frequencies corresponding with these translational and rotational modes can be selected unambiguously based on a mobile block Hessian–PHVA calculation, allowing the prediction of physisorption entropies within an accuracy of  $10\text{--}15 \text{ J mol}^{-1} \text{ K}^{-1}$  as compared to experimental values. The approach presented in this study is useful for studies on other extended catalytic systems.

## 1. INTRODUCTION

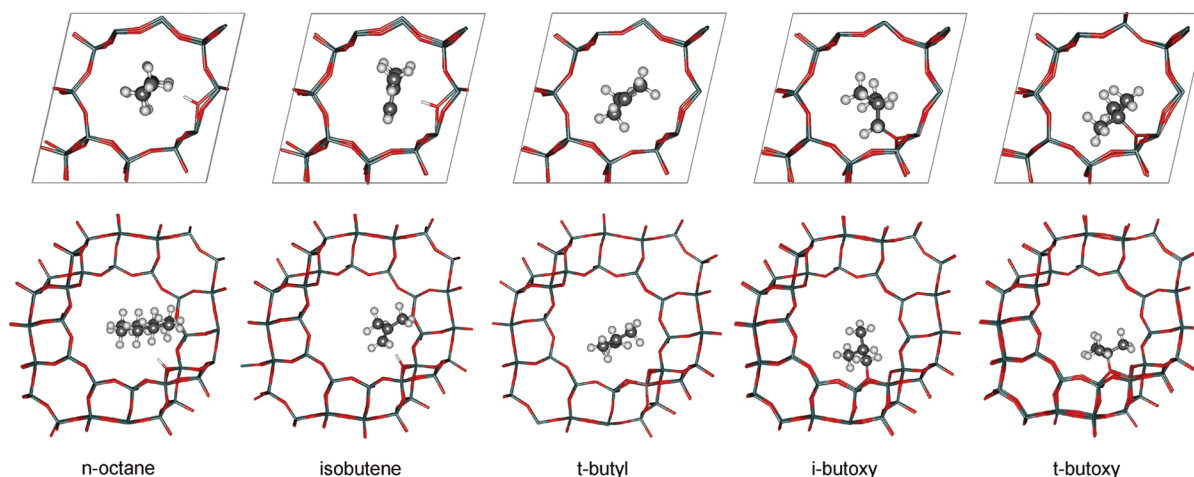
Molecular simulations are a valuable tool to obtain a better understanding of hydrocarbon adsorption and conversion processes in zeolites.<sup>1–21</sup> Nowadays, theoretical calculations on extended zeolite systems are frequently performed as evidenced from the various studies in literature applying quantum mechanical/molecular mechanical (QM/MM),<sup>3–10</sup> QM/QM<sup>11–15</sup> and periodic density functional theory (DFT)<sup>16–21</sup> methods. However, most studies reported in literature only concern electronic energies, while vibrational analysis is usually omitted since it is computationally very demanding. Nonetheless, frequency analysis is part and parcel of the study of hydrocarbon conversion reactions since they are required to calculate the rate and equilibrium coefficients that govern hydrocarbon conversions in practically relevant conditions of temperature and pressure.<sup>22–24</sup> Consequently, criteria for geometry optimization and electronic energy calculation are well established, but the appropriate program settings related to the calculation of harmonic frequencies are less well documented. Nevertheless, a full Hessian vibrational analysis (FHVA) is more and more applied, e.g., in hybrid QM/MM methods.<sup>5,8–10</sup> The combination of a high-level method for a small part of the system and a lower level method for the remainder of the zeolite structure makes a vibrational analysis feasible at a reasonable computational cost. In their hybrid QM/QM approach using the ONIOM method, McCann et al.,<sup>13</sup> Lesthaeghe et al.,<sup>14</sup> and Vandichel et al.<sup>15</sup> applied a partial Hessian vibrational analysis (PHVA)<sup>25–31</sup> on a 46T cluster model of H-ZSM-5, keeping the saturating hydrogen atoms

fixed. In contrast, for periodic DFT methods, very few studies report the extremely time-consuming vibrational analysis. The Hessian, being the second derivatives matrix of the energy with regard to atom displacements, is typically determined via numerical differentiation of the gradient by displacing the atoms, and its calculation thus leads to higher computational costs when the number of atoms in the zeolite unit cell increases. Svelle et al.<sup>12</sup> have studied methylation reactions of ethene, propene, and 2-butene in H-ZSM-5 (289 atoms/unit cell) and calculated the Hessian for a subset of atoms including the hydrocarbon atoms and the 56 zeolite atoms surrounding the acid site. They indicated that this PHVA reduces computational cost by 75% as compared to a FHVA. Tuma and Sauer<sup>20</sup> have performed a FHVA to study the (thermodynamic) stability of various isobutene complexes in H-FER (217 atoms/unit cell).

In this work, we present a periodic DFT study on the physisorption of *n*-octane and isobutene and the chemisorption of *t*-butyl carbenium ion, *i*-butoxy, and *t*-butoxy in H-ZSM-22 and H-FAU; these complexes are representative for the various types of physisorbed and chemisorbed complexes that occur in acid zeolite catalyzed alkane or alkene conversion processes. Figure 1 shows the structures of the various adsorption complexes in H-FAU and H-ZSM-22. We especially focus on the development of a cost-effective procedure for normal-mode analysis (NMA) that yields an acceptable accuracy for the

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**Figure 1.** Physorption and/or chemisorption complexes of n-octane and isobutene in H-ZSM-22 and H-FAU (top and bottom figures, respectively).

calculation of enthalpies, entropies, and the equilibrium coefficients. For example, an accuracy of a factor of 2–6 on the adsorption equilibrium coefficient requires an accuracy of 6–15 J mol<sup>−1</sup> K<sup>−1</sup> on the adsorption entropy. To develop a cost-effective procedure, physisorption and chemisorption entropies resulting from FHVA are compared with results obtained using various PHVA schemes (see Section 2), considering a different number of “free” ( $N_{\text{free}}$ ) or “fixed” ( $N_{\text{fixed}}$ ) atoms for the numerical Hessian calculation. Obviously, a FHVA corresponds to a situation in which all atoms are free, and the gradient is calculated for  $6N$  displaced structures,  $N$  being the total number of atoms in the unit cell. In case some atoms are kept fixed, the construction of the partial Hessian involves calculation of the gradient of  $6N_{\text{free}}$  displaced structures. It is clear that by decreasing the number of free atoms, the vibrational analysis can be speeded up, as also indicated by Svelle et al.<sup>12</sup> The ultimate aim is to select a PHVA scheme with  $N_{\text{free}}$  as small as possible while approaching the accuracy of a FHVA. Physisorption and chemisorption entropies are the ideal quantities to evaluate the accuracy of a PHVA, since they are derived directly from the calculated harmonic frequencies using textbook statistical thermodynamics.<sup>32</sup> The fact that entropies are extremely sensitive to even small variations in low-frequency values (0–100 cm<sup>−1</sup>) makes them even more suited to evaluate the accuracy of PHVA schemes, as these low frequencies are omnipresent in the studied zeolite systems. On the other hand, physisorption and chemisorption enthalpies are much less sensitive to variations in harmonic frequency values and will not be discussed in detail. Previous work has shown that, in the temperature range from 300 to 800 K, the difference between physisorption energies and enthalpies of n-alkanes and alkenes amounts to some 0–5 kJ/mol at most.<sup>9,10</sup>

From the systems studied in this work, physisorbed n-octane and isobutene and chemisorbed *t*-butyl carbenium ion are loosely bonded complexes in H-ZSM-22 and H-FAU zeolites: No chemical bond between the complex and the zeolite is present. In contrast, a C–O bond is formed in the *i*-butoxy and *t*-butoxy alkoxides after protonation of a physisorbed isobutene.

The absence of a direct bond between the adsorbed complex and the zeolite implies a higher translational and rotational mobility of the loosely bonded structures inside the zeolite pores. Previous work has shown that for n-alkanes physisorption

entropy losses calculated from harmonic frequencies only, i.e., the immobile adsorbate method, are overestimated as compared to experimental values.<sup>9,10</sup> Therefore, a mobile adsorbate method has been proposed, in which some of the motions are not treated in the harmonic limit but rather considered to be free translational or rotational motions of the adsorbate in the zeolite pore. In the mobile adsorbate method,<sup>9,10</sup> the partition function is calculated according to eq 1, in which  $q_{\text{immobile}}^{\text{vibr}}$  is the total vibrational partition function (as generally obtained from standard simulation packages), from which the vibrational contribution corresponding to the  $n$  rotational and translational modes is removed ( $q_{nD}^{\text{vibr}}$ ) and replaced by a  $n$ -dimensional ( $nD$ ) free translational and rotational contribution ( $q_{nD}^{\text{trans/rot}}$ ):

$$q_{\text{mobile}} = \frac{q_{\text{immobile}}^{\text{vibr}}}{q_{nD}^{\text{vibr}}} \times q_{nD}^{\text{trans/rot}} \quad (1)$$

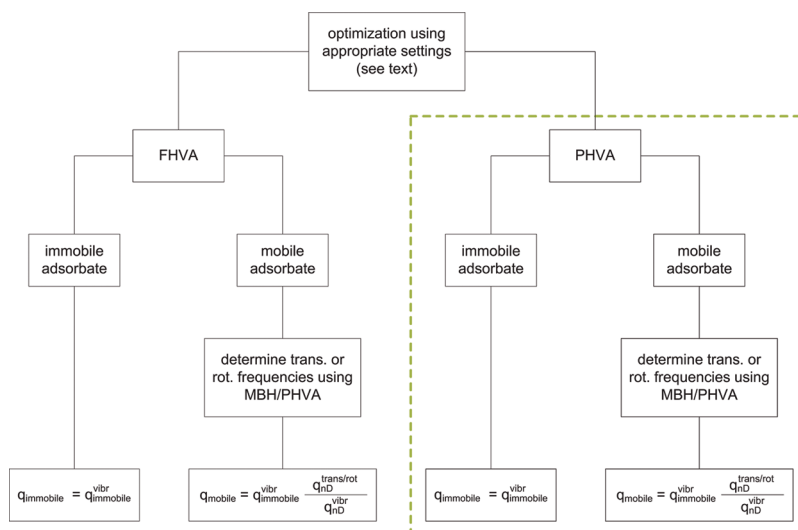
The selection of frequencies corresponding to translational and/or rotational modes is however somewhat ambiguous as it depends on the user's interpretation. In this work, the use of a mobile block Hessian (MBH) based approach to identify these frequencies is explored.

All FHVA calculations have been performed using the Vienna Ab Initio Simulation Package (VASP),<sup>33–36</sup> and postprocessing for PHVA and MBH calculations have been done using the in-house developed software module TAMkin,<sup>37,38</sup> a free python programmed versatile toolkit for normal-mode analysis and chemical kinetics.<sup>31,39–43</sup>

## 2. METHODOLOGY

Figure 2 gives a schematic overview of all types of normal-mode analysis that have been performed in this paper. The following paragraphs comprise a discussion of these different types of methods, i.e., FHVA versus PHVA, the assumption of a mobile versus immobile adsorbate, the use of MBH for an unambiguous selection of translational and rotational modes, and finally the different PHVA schemes.

**Full Hessian versus Partial Hessian Vibrational Analysis.** It is well-known that an FHVA is one of the most time-consuming steps when studying extended systems, such as zeolites. Especially when the Hessian is calculated by numerical differentiation—as is the case for most periodic DFT simulation packages—the



**Figure 2.** Overview of the types of normal-mode analysis that have been performed for the considered physisorption and chemisorption complexes in H-ZSM-22 and H-FAU.

computational effort is significant, due to the large number of atoms in the zeolite unit cell and the calculation of six displacements for each atom. PHVA has the advantage over FHVA that the derivatives with regard to the fixed atoms do not need to be calculated such that in total  $6N_{\text{free}}$  gradient evaluations are required instead of  $6N$ . Many PHVA schemes can be proposed. The different schemes are characterized by the number of fixed atoms and by the particular selection of the fixed atoms. The effect of these parameters on the final outcome is not known for zeolite systems. Not only for small organic systems, such as alcohols and alkanes, but also for large macromolecules, such as proteins, this has been explored before.<sup>31,40–43</sup>

All FHVA and PHVA calculations are performed with TAMkin.<sup>37,38</sup> The TAMkin package loads the second derivatives matrix (Hessian) from the VASP output files. Mass-weighting and diagonalization of the full  $3N \times 3N$  Hessian yields  $3N$  frequencies and normal modes. TAMkin calculates  $3N_{\text{free}}$  PHVA frequencies by first omitting the rows and columns corresponding to fixed atom displacements and next by diagonalizing this smaller Hessian of dimension  $3N_{\text{free}} \times 3N_{\text{free}}$ . No additional Hessian calculations were required to generate all PHVA results in this paper, as all PHVA Hessians could instantaneously be derived from the same FHVA Hessian by TAMkin.<sup>37,38</sup>

**Immobile versus Mobile Adsorbate.** As mentioned in the Introduction, previous work has shown that, for loosely bonded physisorbed complexes, entropy losses calculated based on harmonic frequencies only, i.e., the immobile adsorbate method, are overestimated as compared to experimental values.<sup>9,10</sup> The assumption of an immobile adsorbate conflicts with the significant translational and rotational degrees of freedom of the loosely bonded complex. Therefore a correction scheme, called the mobile adsorbate method, has been proposed (eq 1). The mobile adsorbate method was successfully applied in a study on physisorption of alkanes and alkenes in H-FAU, H-BEA, H-MOR, and H-ZSM-5.<sup>9,10</sup> In eq 1, the partition function of the mobile adsorbate method,  $q_{\text{mobile}}$ , is calculated from the total partition function of the immobile adsorbate method,  $q_{\text{immobile}}$ , in which the contribution  $q_{nD}^{\text{vibr}}$  of the  $n$  harmonic frequencies (typically 3 or 4), corresponding with a translation and/or rotation of the hydrocarbon in the zeolite, is replaced by

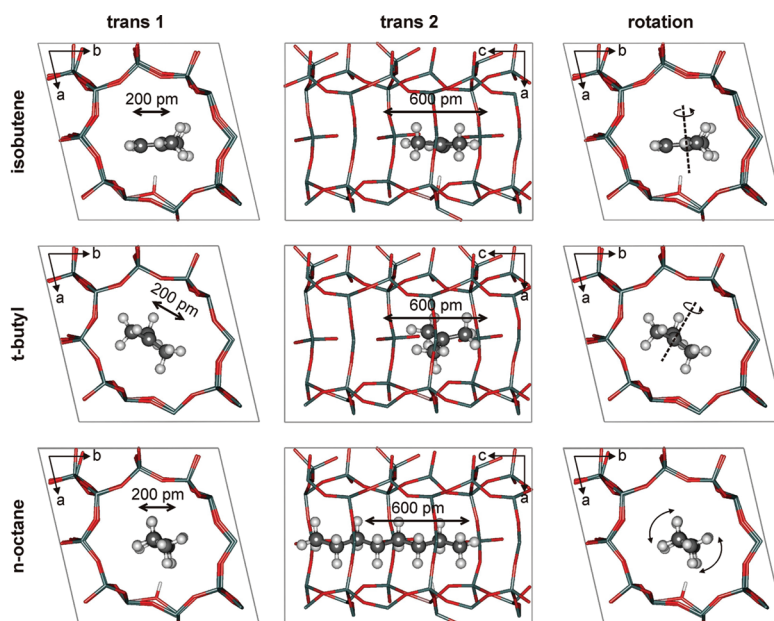
the contribution  $q_{nD}^{\text{trans/rot}}$  of  $n$  free translational and rotational contributions.

The  $n$  degrees of freedom in the mobile adsorbate method are determined from visualization of the FHVA normal modes. More specifically, translations and/or rotations of an adsorbate are considered to be mobile if the following criteria are fulfilled: (1) the harmonic frequencies lie in the range  $0\text{--}100\text{ cm}^{-1}$  and (2) the visualization of the corresponding normal modes shows a translation or rotation of the adsorbate in the zeolite as a whole with only small coupling to internal vibrations of the hydrocarbon or the zeolite. Based on these criteria, we observed the following number of mobile degrees of freedom ( $n$ ): 2D free translation and 1D free rotation ( $n = 3$ ) is assumed for *n*-octane physisorption in H-ZSM-22 and for isobutene physisorption and *t*-butyl chemisorption in both H-ZSM-22 and H-FAU zeolites, while 2D free translation and 2D free rotation ( $n = 4$ ) is assumed for *n*-octane physisorption in H-FAU. The evaluation of the translational partition function requires a “molecular surface area” (analogously to the molecular volume in case of 3D free translation for gas-phase hydrocarbons). This has been chosen as  $200 \times 600\text{ pm}$  and  $800 \times 800\text{ pm}$  for H-ZSM-22 and H-FAU, respectively, according to the available zeolite pore dimensions. Figure 3 illustrates the 2D free translation and the 1D free rotation of the loosely bonded complexes in H-ZSM-22.

Until now, selection of the translational and rotational frequencies is done manually which is somewhat ambiguous and user dependent due to mixing of translational and rotational modes in the low-frequency range. In addition, this work is labor intensive in the case of FHVA calculations in view of the large number of frequencies in the  $0\text{--}100\text{ cm}^{-1}$  range. The MBH approach, in which the hydrocarbon is defined as a rigid block, offers an attractive alternative to this ad-hoc procedure in defining unambiguously these translational and rotational frequencies, as explained in the following section.

**Mobile Block Hessian to Select Translational and Rotational Modes.** In the MBH method, part of the system is grouped into rigid but mobile blocks. During the vibrational analysis, the blocks are allowed to translate or rotate as a whole, such that each block has 6 degrees of freedom (3 translational, 3 rotational), which can be described by 6 so-called block





**Figure 3.** Impression of the 2D free translation and the 1D free rotation of the isobutene, *t*-butyl, and *n*-octane in H-ZSM-22.



















parameters. The internal geometry of the block is kept fixed, which means internal vibrations within the block are not allowed. The number of degrees of freedom of the molecular system is thus reduced from  $3N$  to  $d = 6N_b + N_{\text{free}}$ , where  $N_b$  is the number of blocks and  $N_{\text{free}}$  is the number of free atoms which are not part of any block. Whereas the  $3N$  FHVA frequencies are calculated by mass weighting and diagonalizing the  $3N \times 3N$  full Hessian, the introduction of the block concept requires the diagonalization of the smaller  $d \times d$  MBH. This MBH Hessian consists of the second derivatives matrix of the potential energy with respect to the block parameters and to the coordinates of the free atoms. This MBH matrix can either be calculated by projection of the full Hessian or, if it would be implemented in the simulation package, be directly constructed by well chosen numerical differentiation. After appropriate mass weighting, its diagonalization yields the  $d$  MBH frequencies.<sup>39–43</sup> In this paper, TAMkin is used to calculate the MBH frequencies.<sup>37,38</sup> By making a smart block choice, one can focus on the interesting part of the frequency spectrum.

The combination of the mobile block concept of MBH with fixing zeolite atoms, as in PHVA, allows a more systematic approach to determine the values of  $n$  harmonic frequencies corresponding to the mobile translational and rotational motions of the mobile adsorbate method (see eq 1). In the MBH–PHVA approach in the present study, the zeolite atoms (except acid proton) are kept fixed at their reference position (PHVA concept), while the adsorbate molecule is a mobile block during the vibrational analysis (MBH concept). Whereas initially the  $n$  harmonic frequencies had to be selected out of the  $3N$  FHVA modes, the MBH–PHVA approach reduces this to selecting  $n$  frequencies out of nine frequencies in case of isobutene and *n*-octane physisorption or out of six frequencies in case of chemisorption of the *t*-butyl carbenium ion. Indeed, by fixing all zeolite atoms except the acid proton and considering the adsorbate as a rigid mobile block, only nine frequencies are found from the combined MBH–PHVA approach in the case of physisorption of *n*-octane and isobutene. Three of them correspond to the vibration of the acid proton, and the six other frequencies

mainly correspond to translation and rotation of the hydrocarbon in the zeolite. In case of chemisorption of the *t*-butyl carbenium ion, the deprotonated zeolite is completely fixed, while the carbenium ion is defined as block, resulting in only six frequencies all corresponding to translation or rotation. This significantly simplifies the tedious identification of the  $n$  harmonic frequencies (for the calculation of  $q_{\text{vibr}}^{\text{vibr}}$ ), that are to be replaced by  $n$  free translational and rotational motions ( $q_{\text{immobile}}^{\text{vibr}}$ ) in the mobile adsorbate method (eq 1). As a consequence, not only labor intensive visualization efforts are reduced but also the unambiguous identification of the  $n$  harmonic frequencies now becomes possible, since coupling with internal zeolite or hydrocarbon vibrations is excluded.

**FHVA and Considered PHVA Schemes.** A schematic overview of the FHVA and the various PHVA schemes considered in this work is shown in Figure 4. Case A represents the FHVA calculation: all atoms are considered free for the vibrational analysis in the gas-phase hydrocarbon, the unloaded zeolite and the zeolite–adsorbate system, i.e., six displacements for each atom are considered for the numerical Hessian calculation. Case B groups all PHVA calculations, with the number of free atoms ( $N_{\text{free}}$ ) ranging from a few (B.[ $N_{\text{free}}$  low]) to almost all zeolite atoms free (B.[ $N_{\text{free}}$  high]). In cases A and B, hydrocarbon atoms are always considered free. Comparison of cases A and B allows the evaluation of the accuracy of the various PHVA schemes for the calculation of the physisorption and chemisorption entropies for the studied systems. Cases C and D are analogous to case A and B, but the hydrocarbon is defined as a mobile block without internal degrees of freedom. Comparison of the cases C and D with their analogues in cases A and B allows the assessment of the contribution of the internal hydrocarbon vibrations to the physisorption and chemisorption entropies in H-ZSM-22 and H-FAU.

Many different PHVA schemes have been included in this study. Table 1 summarizes all different choices, mentioning the name, the number of free and fixed zeolite atoms and the number of free or fixed T (Al or Si) atoms is mentioned between brackets. Starting from one free zeolite atom, i.e., the acid proton, we gradually increased the number of free Si or O atoms around the

Scheme	Type of Calculation	hydrocarbon	zeolite	hydrocarbon + zeolite
A	FHVA			
		FHVA	FHVA	FHVA
B.[N <sub>free</sub> high]	PHVA			
		FHVA	PHVA	PHVA
B.[i]	PHVA	...	...	...
		...	...	...
B.[N <sub>free</sub> low]	PHVA			
		FHVA	PHVA	PHVA
C	MBH-FHVA			
		MBH	FHVA	MBH-FHVA
D.[N <sub>free</sub> high] <sup>MBH</sup>	MBH-PHVA			
		MBH	PHVA	MBH-PHVA
D.[i] <sup>MBH</sup>	MBH-PHVA	...	...	...
		...	...	...
D.[N <sub>free</sub> low] <sup>MBH</sup>	MBH-PHVA			
		MBH	PHVA	MBH-PHVA

**Figure 4.** Schematic representation of the FHVA and PHVA cases considered in this work. Fixed parts of the system are indicated black, while the mobile blocks are shaded. Case A represents the FHVA method, while B.[N<sub>free</sub> high] (almost all atoms free) to B.[N<sub>free</sub> low] (almost all atoms fixed) corresponds to all PHVA schemes considered. Cases C and D are similar to A and B but with a mobile block description of the hydrocarbon (see text).

acid site to finally end up with a zeolite unit cell for which all zeolite atoms are considered free. Details on the various PHVA schemes used are given in Supporting Information.

The PHVA choices are labeled by the notation  $[N_{\text{free}}^{\text{zeo}}, N_{\text{fixed}}^{\text{zeo}}]$  indicating the number of free ( $N_{\text{free}}^{\text{zeo}}$ ) and fixed ( $N_{\text{fixed}}^{\text{zeo}}$ ) zeolite atoms; all hydrocarbon atoms are free in case of FHVA or PHVA. An index (a, b, or c) is added if different schemes exist with the same number of free and fixed zeolite atoms but with different selections of atoms. For example, for H-ZSM-22 (see Section 3) in the [1,108] scheme, 1 zeolite atom (in this case the acid proton) is free, and the other 108 H-ZSM-22 zeolite atoms are fixed. Also for H-ZSM-22, in scheme [43,66], 43 zeolite atoms are free, while 66 atoms are fixed. Note that the schemes [109,0] and [145,0], respectively, H-ZSM-22 and H-FAU (see Section 3), correspond to the FHVA case (all atoms free, 0 atoms fixed). When MBH–FHVA or MBH–PHVA is applied, in which the hydrocarbon is modeled as a mobile rigid block, the scheme is denoted as  $[N_{\text{free}}^{\text{zeo}}, N_{\text{fixed}}^{\text{zeo}}]^{\text{MBH}}$ .

### 3. COMPUTATIONAL DETAILS

**Investigated Systems.** Physisorption of n-octane and of isobutene and chemisorption of isobutene in both H-ZSM-22

**Table 1.** Different PHVA Schemes Considered in This Study for H-ZSM-22 and H-FAU<sup>a</sup>

H-ZSM-22 PHVA scheme	$N_{\text{free}}^{\text{zeo}}$ ( $T_{\text{free}}$ )		$N_{\text{fixed}}^{\text{zeo}}$ ( $T_{\text{fixed}}$ )	
[1,108]	1	(0)	108	(36)
[8,101]	8	(4)	101	(32)
[16,93]	16	(8)	93	(28)
[28,81]	28	(14)	81	(22)
[43,66] <sup>a</sup>	43	(6)	66	(30)
[43,66] <sup>b</sup>	43	(20)	66	(16)
[58,51]	58	(22)	51	(14)
[67,42]	67	(30)	42	(6)
[82,27]	82	(32)	27	(4)
[106,3]	106	(33)	3	(3)
[107,2] <sup>a</sup>	107	(33)	2	(3)
[107,2] <sup>b</sup>	107	(33)	2	(3)
[107,2] <sup>c</sup>	107	(34)	2	(2)
[108,1] <sup>a</sup>	108	(35)	1	(1)
[108,1] <sup>b</sup>	108	(35)	1	(1)
[108,1] <sup>c</sup>	108	(36)	1	(0)
[109,0]	109	(36)	0	(0)
H-FAU PHVA scheme	$N_{\text{free}}^{\text{zeo}}$ ( $T_{\text{free}}$ )		$N_{\text{fixed}}^{\text{zeo}}$ ( $T_{\text{fixed}}$ )	
[1,144]	1	(0)	144	(48)
[6,139]	6	(3)	139	(45)
[19,126]	19	(8)	126	(40)
[26,119]	26	(11)	119	(37)
[38,107]	38	(16)	107	(32)
[55,90]	55	(24)	90	(24)
[100,45]	100	(40)	45	(8)
[105,40]	105	(40)	40	(8)
[142,3]	142	(45)	3	(3)
[143,2] <sup>a</sup>	143	(46)	2	(2)
[143,2] <sup>b</sup>	143	(46)	2	(2)
[143,2] <sup>c</sup>	143	(48)	2	(0)
[144,1] <sup>a</sup>	144	(47)	1	(1)
[144,1] <sup>b</sup>	144	(47)	1	(1)
[144,1] <sup>c</sup>	144	(48)	1	(0)
[145,0]	145	(48)	0	(0)

<sup>a</sup>The different schemes are labeled as  $[N_{\text{free}}^{\text{zeo}}, N_{\text{fixed}}^{\text{zeo}}]$ , mentioning the number of free zeolite atoms ( $N_{\text{free}}^{\text{zeo}}$ ) and the number of fixed ( $N_{\text{fixed}}^{\text{zeo}}$ ) zeolite atoms; the number of free or fixed T (Al or Si) atoms is mentioned between brackets.

and H-FAU have been studied. The unit cells of H-ZSM-22 and H-FAU are sufficiently small to compute the benchmark full Hessian at a reasonable computational cost. H-ZSM-22 is a medium-pore zeolite characterized by 10-membered ring channels and has a cell composition  $\text{Si}_{33}\text{AlO}_{72}\text{H}$ . The optimized unit cell parameters are  $a = 1132.9$  pm,  $b = 1130.8$  pm,  $c = 1542.8$  pm,  $\alpha = 90.14^\circ$ ,  $\beta = 90.07^\circ$ , and  $\gamma = 77.04^\circ$ . H-FAU is a large-pore zeolite characterized by supercages connected by 12-membered rings, has a cell composition  $\text{Si}_{47}\text{AlO}_{96}\text{H}$ , and is characterized by the unit cell parameters  $a = 1740.1$  pm,  $b = 1736.2$  pm,  $c = 1742.4$  pm,  $\alpha = 59.88^\circ$ ,  $\beta = 59.82^\circ$ , and  $\gamma = 59.87^\circ$ . Calculated physisorption entropies for n-octane and isobutene in H-ZSM-22 and H-FAU are compared with experimental and simulation data from literature.<sup>9,10,44–46</sup> Figure 1 depicts the different studied adsorption complexes in H-ZSM-22 and H-FAU.

**Table 2.** Geometry Optimization Criteria for the Zeolite, the Physisorbed *n*-Octane and Isobutene, and the Chemisorbed *t*-Butyl Carbenium Ion, *i*-Butoxy Alkoxide and *t*-Butoxy Alkoxide in H-ZSM-22 and H-FAU<sup>a</sup>

	H-ZSM-22			H-FAU		
	$E_{\text{cutoff}}$ (eV)	$\Delta E_{\text{SCF}}$ (eV)	max force (eV/Å)	$E_{\text{cutoff}}$ (eV)	$\Delta E_{\text{SCF}}$ (eV)	max force (eV/Å)
zeolite	400	$10^{-8}$	0.010	400	$10^{-8}$	0.010
<i>n</i> -octane	600	$10^{-10}$	0.010	—	—	—
<i>i</i> -butene	600	$10^{-10}$	0.015	400	$10^{-8}$	0.015
<i>t</i> -butyl	400	$10^{-8}$	0.015	—	—	—
<i>i</i> -butoxy	400	$10^{-8}$	0.020	400	$10^{-10}$	0.010
<i>t</i> -butoxy	400	$10^{-8}$	0.020	400	$10^{-8}$	0.015

<sup>a</sup> The used plane-wave energy cutoff  $E_{\text{cutoff}}$ , the SCF loop convergence criterion  $\Delta E_{\text{SCF}}$ , and the maximum force on the atoms are given.

**Periodic DFT Calculations.** Periodic DFT calculations are performed using VASP.<sup>33–36</sup> The total energy is calculated solving the Kohn–Sham equations of DFT using the gradient-corrected functionals of Perdew and Wang 91 (PW91) as the exchange–correlation functional.<sup>47</sup> The calculations are performed using the projector-augmented wave (PAW) method. This method was originally developed by Blöchl<sup>48</sup> and was adapted by Kresse and Joubert.<sup>49</sup> In general, a plane-wave cutoff of 400 eV was used in the calculations, and the Brillouin zone sampling was restricted to the  $\Gamma$  point.

Adsorption complexes are optimized in two steps. First, the conjugate gradient minimization algorithm was used to obtain a preoptimized structure until forces dropped below 0.05 eV/Å. Second, a quasi-Newton algorithm is employed to further optimize the structure until the maximum forces on the atoms are at least lower than 0.02 eV/Å. The loop for solving the electronic self-consistent field (SCF) equations iteratively is stopped when the difference between two consecutive energies is such that the accuracy of the energy is of the order of  $10^{-8}$  eV.

After optimization of the adsorption complexes, a FHVA has been performed for all structures: The Hessian is calculated numerically by imposing positive and negative displacements in the *x*, *y*, and *z*-directions ( $\Delta = 0.015$  Å) on each atom. We always carefully checked that no unwanted imaginary frequencies were present, ensuring a minimum-energy structure. However, especially in the case of loosely bonded complexes, such as physisorption of *n*-octane and isobutene, unwanted imaginary frequencies may appear when using the above-mentioned standard optimization settings (energy cutoff 400 eV, maximum force 0.02 eV/Å, and SCF loop convergence criteria  $10^{-8}$  eV). In these cases, tighter VASP settings were necessary to get rid of the spurious imaginary frequencies: (i) maximum force on the atoms down to 0.01 eV/Å, (ii) SCF loop convergence criteria down to  $10^{-10}$  eV, and (iii) plane-wave energy cutoff up to 600 eV. Especially the increase of the plane wave energy cutoff was found to be crucial to ensure the absence of unwanted imaginary frequencies. Table 2 summarizes the used settings for the optimization of each of the studied structures. In the statistical thermodynamics postprocessing, no frequency scaling factor was used for the calculation of the physisorption and chemisorption entropies.

For the loosely bonded *n*-octane and *t*-butyl carbenium ion complexes in H-FAU, spurious imaginary frequencies were still present even when using the most stringent optimization criteria. Many different configurations of the hydrocarbon inside the H-FAU zeolite have been considered, and even reoptimization of the structures using a cutoff energy of 600 eV, SCF loop convergence criteria of  $10^{-12}$  eV, and maximum forces on the

atoms of 0.004 eV/Å was unsuccessful. The potential energy surface of such loosely bonded adsorbates is very flat, which makes the calculations extremely sensitive to numerical noise. More details on these calculations can be found in Supporting Information. In these cases of unwanted imaginary frequencies, no further processing of the Hessian was performed, and therefore, the physisorbed *n*-octane and the chemisorbed *t*-butyl carbenium ion complexes in H-FAU are not further investigated in this study.

#### 4. RESULTS AND DISCUSSION

As mentioned in the Introduction, the focus of this work is on physisorption and chemisorption entropies and not on physisorption and chemisorption enthalpies. First, FHVA and PHVA results are compared assuming an immobile adsorbate, i.e., the approach in which all harmonic frequencies also those corresponding to translation and rotation, are retained. Next, the mobile adsorbate method and the application of the MBH method for an unambiguous determination of translational and rotational frequencies are discussed for the loosely bonded complexes. Finally, inspired by the conclusions of this work, some general guidelines for performing vibrational analysis of extended systems are presented.

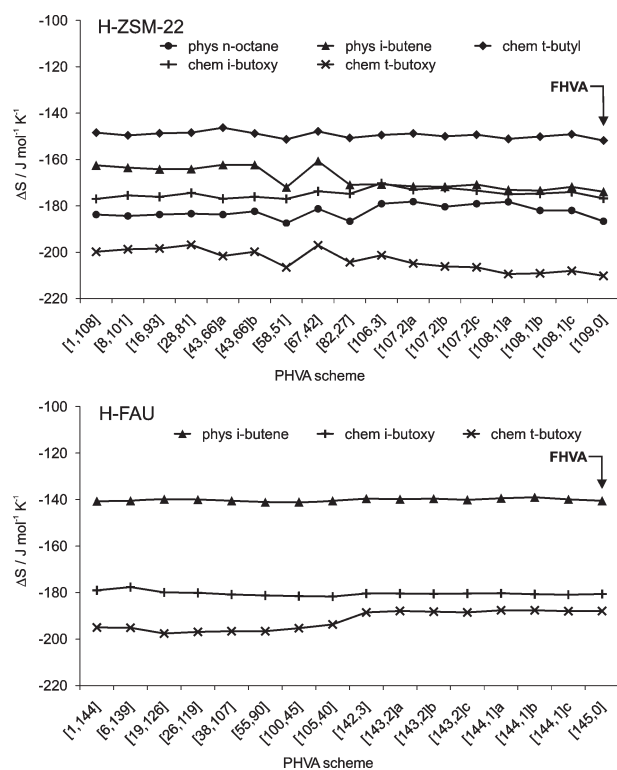
For completeness, the calculated physisorption and chemisorption enthalpies at 300 K for the studied complexes can be found in Supporting Information (Table S.1). Note that these enthalpy differences are independent of the PHVA scheme applied and equal to the FHVA results.

**FHVA versus PHVA Assuming an Immobile Adsorbate.** *FHVA Zero Frequencies.* In principle, FHVA calculations should yield three zero frequencies corresponding to the translation of the zeolite unit cell as a whole. In practice, very low frequencies are found for these motions of the unit cells, and the obtained values can be regarded as indication for the quality of the Hessian. Table 3 shows that the obtained imaginary frequencies have values between  $-1.5$  and  $-6.0$   $\text{cm}^{-1}$  indicative of a well-conditioned Hessian considering the numerical calculation as implemented in VASP.

*FHVA and PHVA Adsorption Entropies.* Figure 5 shows the calculated physisorption and chemisorption entropies in H-ZSM-22 and H-FAU, respectively, assuming an immobile adsorbate for FHVA and the various PHVA schemes. The numerical values are given in the Supporting Information (Tables S.2 and S.3). In Figure 5, the PHVA scheme with only one free zeolite atom, i.e., the zeolite acidic H-atom, scheme [1,108] in H-ZSM-22 and scheme [1,144] in H-FAU, is found at the most left and the FHVA benchmark result at the most right of the abscis.

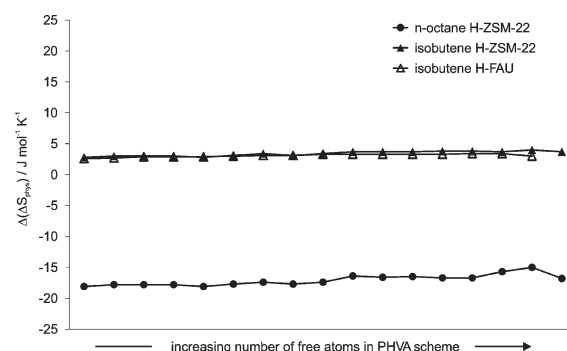
**Table 3.** Zero Frequencies Corresponding to the Translation of the Zeolite Unit Cell as an Indication of the Quality of the Hessian<sup>a</sup>

zero frequencies (cm <sup>-1</sup> )	H-ZSM-22			H-FAU		
zeolite	-2.4	-1.9	-1.6	-2.3	-2.1	-1.8
phys n-octane	-4.3	-2.0	-1.5	—	—	—
phys <i>i</i> -butene	-5.5	-4.5	-3.4	-2.8	-1.3	-1.3
chem <i>i</i> -butoxy	-6.4	-5.3	-3.1	-1.4	-1.4	-1.3
chem <i>t</i> -butoxy	-5.1	-3.8	-3.5	-3.6	-2.5	-2.0
chem <i>t</i> -butyl	-6.0	-4.6	-3.6	—	—	—

<sup>a</sup> Imaginary frequencies are denoted with a minus sign.**Figure 5.** Physisorption and chemisorption entropies of n-octane, isobutene, *t*-butyl carbenium ion, *i*-butoxy and/or *t*-butoxy in H-ZSM-22 (top) and H-FAU (bottom) calculated with the immobile adsorbate method for FHVA and various PHVA schemes.

FHVA physisorption entropies of, respectively, n-octane and isobutene in H-ZSM-22 amount to  $-189$  and  $-174 \text{ J mol}^{-1} \text{ K}^{-1}$ , while FHVA chemisorption entropies for the *t*-butyl carbenium ion, and the *i*-butoxy, and *t*-butoxy alkoxides are  $-152$ ,  $-177$ , and  $-210 \text{ J mol}^{-1} \text{ K}^{-1}$ . In H-FAU on the other hand, FHVA physisorption and chemisorption entropies of isobutene, *i*-butoxy, and *t*-butoxy, respectively, are  $-141$ ,  $-181$ , and  $-188 \text{ J mol}^{-1} \text{ K}^{-1}$ . Entropy losses in H-FAU are somewhat lower as compared to H-ZSM-22 in accordance with the more open structure of H-FAU.

Comparison of FHVA with physisorption and chemisorption entropies calculated with the various PHVA schemes shows that all FHVA and PHVA results fall within a narrow range of approximately  $10 \text{ J mol}^{-1} \text{ K}^{-1}$  for H-ZSM-22 as well as for H-FAU. In addition, no systematic trends in the deviation are

**Figure 6.** Deviations  $\Delta(\Delta S_{\text{phys}})$  caused by neglecting the internal vibrations of the hydrocarbon for the FHVA and various PHVA schemes.

observed with increasing PHVA scheme size. The tighter convergence criteria for loosely bonded physisorption complexes (see Table 2) are needed to ensure this relatively small range. For instance, optimization of the n-octane and isobutene physisorption complexes in H-ZSM-22 using the standard settings (energy cutoff 400 eV, SCF convergence criterion  $10^{-8} \text{ eV}$ ) lead to differences of physisorption entropies between FHVA and PHVA up to  $30 \text{ J mol}^{-1} \text{ K}^{-1}$  (see Figure S.1, Supporting Information). This can be understood from the presence of floppy modes for the loosely bond complexes: The small energy changes upon atom displacements result in low-lying frequencies which are easily contaminated with noise if less stringent convergence criteria are used for the plane-wave energy cutoff and the SCF convergence criterion.

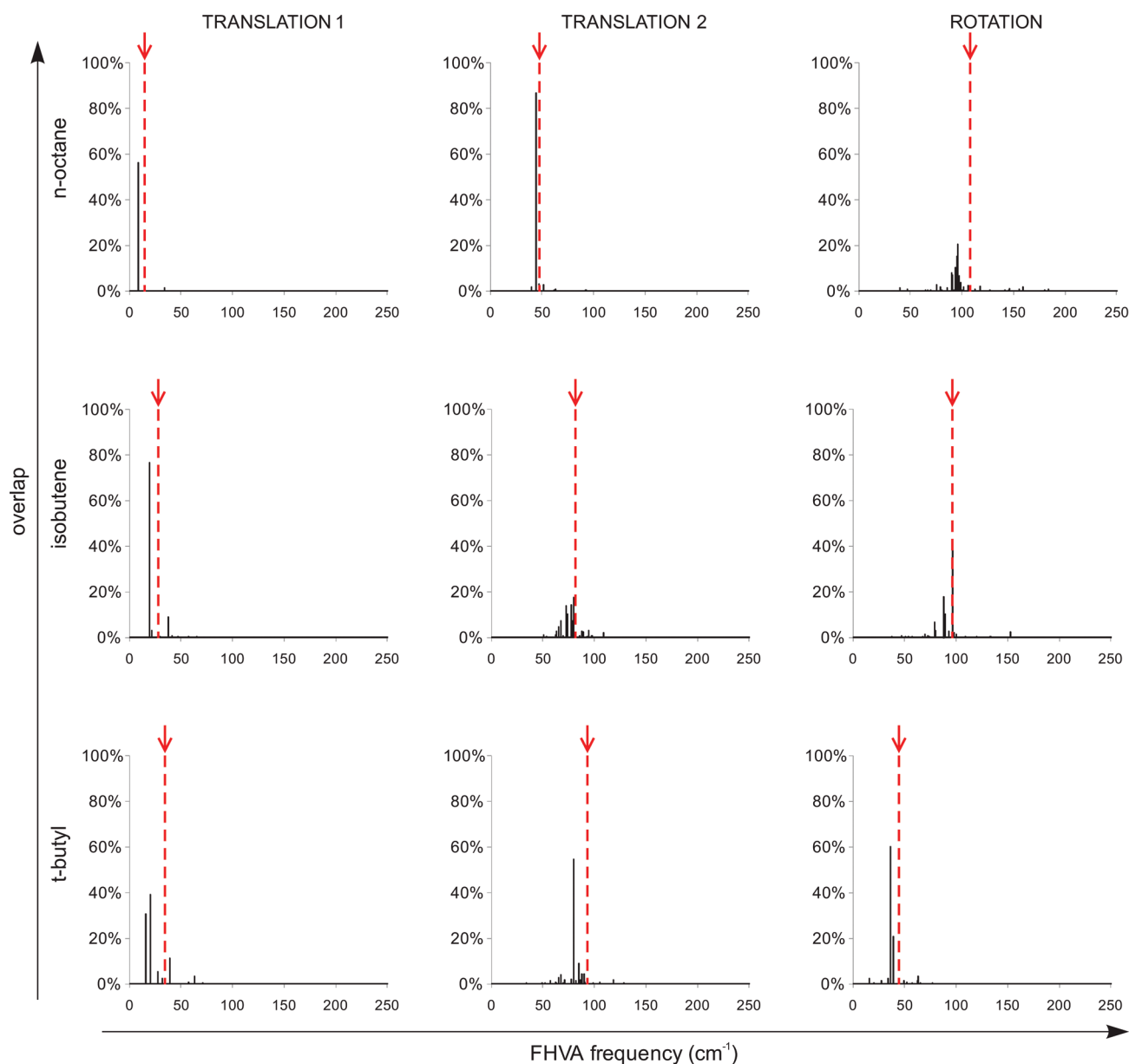
The most striking conclusion however is that a PHVA calculation in its most simplified form, i.e., with only the zeolite acid H-atom considered free, yields similar physisorption and chemisorption entropies than a computationally much more expensive FHVA calculation. This implies that the internal zeolite vibrations have only a limited impact to the adsorption entropy, whereas the main contribution stems from the frequencies describing the internal vibrations in the hydrocarbon complex and/or the vibrations of the hydrocarbon relative to the zeolite. Apparently, only a small part of the extended zeolite catalyst needs to be considered for a high-quality vibrational analysis, yielding results comparable to a FHVA. This observation opens perspectives for other extended systems beyond zeolites, provided the simulation software allows the calculation of partial Hessians. The geometry of large systems can be fully or partially optimized at a high level of theory, while the vibrational analysis can be limited to subset of atoms, making this computationally demanding step considerably more feasible. The speedup can be roughly estimated to be

$$N/N_{\text{free}} \quad (2)$$

in which  $N$  and  $N_{\text{free}}$ , respectively, are the total number of atoms and the number of free atoms in the unit cell, obviously accounting for the zeolite as well as the hydrocarbon atoms.

**Influence of the Internal Vibrations of the Hydrocarbon.** The influence of the internal hydrocarbon vibrations on the physisorption entropies of n-octane and isobutene in H-ZSM-22 and H-FAU is evaluated by comparing cases A with C and cases B.[i] with D.[i] (see Figure 4). In cases C and D, the hydrocarbon is considered as a mobile block such that its internal vibrations are absent in these models. Figure 6 shows the calculated differences





**Figure 7.** Overlap for the two translational modes and one rotational mode for *n*-octane (top), isobutene (middle), and *t*-butyl carbenium (bottom) in H-ZSM-22, as obtained from  $[1,108]^{\text{MBH}}$ , with the FHVA calculated modes (scheme  $[109,0]$ ) in H-ZSM-22. The red dashed line, indicated by the arrow, represents the unique translational, respectively, rotational frequency obtained from the  $[1,108]^{\text{MBH}}$  calculation. The overlap of the corresponding mode with the FHVA modes is indicated by the black lines spectrum.

$\Delta(\Delta S_{\text{phys}})$  of the physisorption entropies, caused by neglecting the internal hydrocarbon vibration. For FHVA,  $\Delta(\Delta S_{\text{phys}})$  is calculated as follows:

$$\Delta(\Delta S_{\text{phys}}) = \Delta S_{\text{phys}}^{\text{case A}} - \Delta S_{\text{phys}}^{\text{case C}} \quad (3)$$

In case of PHVA,  $\Delta(\Delta S_{\text{phys}})$  is calculated as

$$\Delta(\Delta S_{\text{phys}}) = \Delta S_{\text{phys}}^{\text{case B.[i]}} - \Delta S_{\text{phys}}^{\text{case D.[i]}} \quad (4)$$

Figure 6 shows that the internal vibrational entropy of isobutene has only a minor contribution to the adsorption entropy since the calculated differences  $\Delta(\Delta S_{\text{phys}})$  amount to about  $3\text{--}4 \text{ J mol}^{-1} \text{ K}^{-1}$  in H-ZSM-22 as well as in H-FAU. Gas-

phase isobutene is a rather small molecule, and no frequencies lower than  $100 \text{ cm}^{-1}$ , which contribute most to the entropy, are present. The lowest frequencies of  $173$  and  $208 \text{ cm}^{-1}$  correspond to the (anti)symmetric methyl rotation. Consequently, considering isobutene as a mobile block has only a minor influence on the physisorption entropy. In contrast, gas-phase *n*-octane is much more flexible and subject to many low-frequency motions; 3 frequencies are lower than  $100 \text{ cm}^{-1}$ , the most pronounced one being an internal rotation at  $43 \text{ cm}^{-1}$ . Since these internal rotations are rather hindered when the *n*-octane molecule is physisorbed in the zeolite pores, the contributions to the entropy do not cancel out, and  $\Delta(\Delta S_{\text{phys}})$  amounts to  $-14$  to  $-18 \text{ J mol}^{-1} \text{ K}^{-1}$  in the case of *n*-octane adsorption in H-ZSM-22. It can thus be expected that for hydrocarbons with many possible



**Table 4. Immobile versus Mobile Physisorption and Chemisorption Entropies of n-Octane, Isobutene, and *t*-Butyl Carbenium Ion Calculated with FHVA<sup>a</sup>**

(J mol <sup>-1</sup> K <sup>-1</sup> )	H-ZSM-22		H-FAU		gas phase	
	immobile	mobile	immobile	mobile	3D trans	3D rot
n-octane	-189	-148	—	—	168	117
isobutene	-174	-126	-141	-94	159	96
<i>t</i> -butyl	-152	-102	—	—	159	104

<sup>a</sup> The translational and rotational contributions to the entropy of the gas-phase hydrocarbons are added as a reference.

internal rotations in gas phase, such as long n-alkanes (like n-octane in this case), MBH-FHVA (C) or MBH-PHVA (D.[i]) calculations yield significantly different physisorption entropies as compared to FHVA (A) or PHVA (B.[i]).

**Immobile versus Mobile Adsorbate.** *MBH-PHVA-Based Selection of Translational and Rotational Frequencies — overlap with FHVA spectrum.* As explained in Section 2, MBH-PHVA schemes [1,108]<sup>MBH</sup> in H-ZSM-22 and [1,144]<sup>MBH</sup> in H-FAU are applied for the identification of translational and rotational frequencies of loosely bonded complexes. The overlap of an MBH-PHVA mode with an FHVA mode is defined as the absolute value of the dot product of the normalized MBH-PHVA mode with the normalized FHVA mode, such that it lies in the range 0–1. A high overlap value indicates that the MBH-PHVA and the FHVA modes represent similar motions. Since the MBH-PHVA modes represent translational and rotational motions of the hydrocarbon in the zeolite pore, overlaps of the MBH-PHVA modes with all FHVA modes are adequate parameters to identify the translational and rotational motions in the FHVA spectrum. This is shown in Figure 7 for physisorption of n-octane and isobutene and chemisorption of the *t*-butyl carbenium ion in H-ZSM-22. The dashed line, indicated by the arrow, represents the unique translational or rotational frequency obtained from the MBH-PHVA calculation. The black line spectrum illustrates the mixing of the translational and rotational modes over several frequencies in the FHVA calculation, also revealing the ambiguity when translational and rotational frequencies are selected manually from the FHVA calculations. A similar figure for the physisorption of isobutene in H-FAU can be found in the Supporting Information (Figure S.2). Figure 7 also shows that the unique translational and rotational frequencies of the MBH-PHVA approach correspond reasonably well to the frequency spectrum obtained from the FHVA calculations. The frequency values are slightly higher, as expected in view of the large part of the zeolite that is kept fixed in the MBH-PHVA calculation, thus constraining the remaining motions.

**FHVA and PHVA Adsorption Entropies.** Table 4 compares the immobile and mobile adsorbate method for the FHVA calculation of the physisorption entropies of n-octane and isobutene and the chemisorption entropy of the *t*-butyl carbenium ion. The 3D and 3D rotational entropies of the molecules in the gas phase are added, since the gas-phase translational/rotational entropy can be regarded as a rough (but incorrect) estimate for the adsorption entropies.<sup>9</sup>

The mobile adsorbate method as described in eq 1 has been applied, using the translational and rotational frequencies obtained from the MBH-PHVA approach explained in the previous paragraph. Because of the replacement of vibrational

**Table 5. Comparison of Our Calculated Values for the Physisorption Entropy of n-Octane (Mobile Adsorbate) with Values Reported in Literature**

(J mol <sup>-1</sup> K <sup>-1</sup> )	H-ZSM-22	H-FAU
n-octane		
this work	-148	—
Denayer et al. <sup>45,46a</sup>	-159	-83 to -98
Eder et al. <sup>44</sup>	—	-101
De Moor et al. <sup>9</sup>	—	-88
isobutene		
this work	-126	-94
De Moor et al. <sup>9</sup>	—	-100

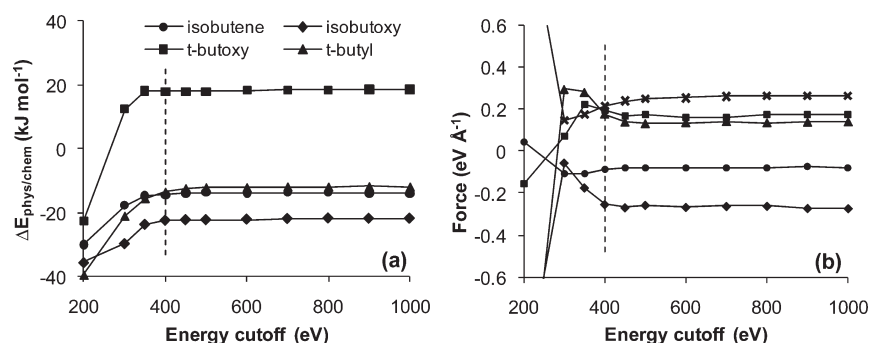
<sup>a</sup> Values have been revisited, see De Moor et al.<sup>10</sup>

contributions by free translational and free rotational contributions, entropy losses upon adsorption become smaller. A shift of about 50 J mol<sup>-1</sup> K<sup>-1</sup> is observed for the entropies, assuming an immobile versus a mobile adsorbate. Mobile adsorbate physisorption and chemisorption entropies for n-octane, isobutene, and *t*-butyl carbenium ion amount to -148, -126, and -102 J mol<sup>-1</sup> K<sup>-1</sup> in H-ZSM-22, while the physisorption entropy for isobutene amounts to -94 J mol<sup>-1</sup> K<sup>-1</sup> in H-FAU. As already mentioned above, the entropy loss upon isobutene physisorption is somewhat higher in H-ZSM-22 than in H-FAU, due to the more confined structure of the former.

The immobile–mobile adsorbate entropy shift is independent of the FHVA or PHVA scheme, and as a consequence, PHVA and FHVA results are nearly identical and differ at most 10 J mol<sup>-1</sup> K<sup>-1</sup>, as was also the case for the immobile adsorbate method. Fluctuations observed in the immobile adsorbate method are also present in the mobile adsorbate method (see Figure 5). There are no systematic trends, and PHVA schemes with only one free zeolite atom, [1,108] (H-ZSM-22) and [1,144] (H-FAU), yield values that are very similar to the FHVA results. An uncertainty of 10 J mol<sup>-1</sup> K<sup>-1</sup> on the physisorption or chemisorption entropy leads to an uncertainty of a factor 3 on the adsorption equilibrium coefficient, which is very acceptable. Figures presenting the effect of PHVA assuming a mobile adsorbate, analogous to Figure 5, are given in the Supporting Information (Figures S.3 and S.4) as well as the numerical values for the physisorption and chemisorption entropies (Tables S.2 and S.3, Supporting Information).

**Comparison with Experiment.** In Table 5, FHVA physisorption entropies for n-octane and isobutene in H-ZSM-22 and H-FAU, assuming a mobile adsorbate, are compared with experimental values and values reported for other molecular simulations from literature. A very good agreement is observed between the VASP physisorption entropies calculated in this work and the experimental values determined by Denayer et al.<sup>45,46</sup> Our VASP calculated physisorption entropies also nicely agree with QM-Pot(MP2//B3LYP) physisorption entropies reported by De Moor et al.<sup>9</sup> The good agreement between these two different simulation methods for the physisorption of isobutene in H-FAU indicates that the influence of the van der Waals stabilizing interactions—these are adequately described by QM-Pot(MP2//B3LYP) but not by VASP—on the value of the entropies is rather limited for the zeolite systems under study.

Differences between our calculated physisorption entropies and the literature data do not exceed 10–15 J mol<sup>-1</sup> K<sup>-1</sup>. One of the possible explanations for the differences between the simulation and the experimental results may relate to the improper



**Figure 8.** Influence of energy cutoff (a) on the physisorption/chemisorption energy and (b) on the gradient of some arbitrarily chosen atoms of a nonoptimized isobutene, *i*-butoxy, *t*-butoxy, and *t*-butyl complexes in H-ZSM-22.

description of internal frustrated rotational modes by the harmonic oscillator approximation; such a refinement of the approach can be the topic of a further thorough study.

#### Guidelines for Vibrational Analysis of Extended Systems.

From our results, we can state that the use of PHVA (indicated by the dashed line in Figure 2) for zeolite systems, and by extension for other catalytic systems, leads to a significant and structural reduction of the computational resources needed. Evidently, this advantageous use of PHVA is only possible with simulation packages in which the partial Hessian calculation is implemented, as is the case in VASP.<sup>33–36</sup> For loosely bonded complexes, such as physisorbed alkanes or alkenes and carbenium ions, the mobile adsorbate method is proposed, with an unambiguous selection of the translational or rotational modes based on an MBH–PHVA calculation using TAMkin.<sup>37,38</sup> As discussed below, a well-conditioned Hessian is however in any case required.

Based on this study on the physisorption and chemisorptions of *n*-octane and isobutene in H-ZSM-22 and H-FAU, some guidelines can be formulated for performing geometry optimization and vibrational analysis on extended zeolite systems using VASP.<sup>33–36</sup> Strategies and settings for electronic energy calculations of extended zeolite systems are well established. However, commonly used convergence criteria sufficiently accurate for a geometry optimization appear not to be sufficiently tight for successful normal-mode analysis; frequently, unwanted imaginary frequencies are present, in particular for loosely bonded physisorption complexes. Stricter optimization criteria are thus necessary to construct a well-conditioned Hessian, further compounding the computational cost of the numerical Hessian calculations. As illustrated in this study, this drawback can be largely overcome by using PHVA schemes. Indeed, it has been shown that for the systems considered in this study, even if only the zeolite acid H-atom is considered to be free, the PHVA results are very similar to the computationally much more expensive FHVA results. A deviation from the FHVA adsorption entropy of  $10 \text{ J mol}^{-1} \text{ K}^{-1}$  at most has been found. This is a very important conclusion, in view of the fact that a full vibrational analysis is in general much more time-consuming than a geometry optimization using more stringent convergence criteria. From the theoretical speed-up that can be calculated using eq 2, it is concluded that the [1,108] PHVA scheme is some 9 times faster than FHVA for isobutene physisorption in H-ZSM-22, i.e., the computational cost is reduced by 89%. In H-FAU, the [1,144] PHVA scheme is even 12 times faster, leading to a reduction of the computational cost of 92%. Illustrating figures can be found in the Supporting Information. Clearly, these schemes are computationally very

attractive for normal-mode analysis of extended zeolite structures.

Although for studies of zeolite systems using VASP an energy cutoff of 400 eV is widely accepted, we have shown that a cutoff of 600 eV was necessary for some loosely bonded physisorption complexes. Figure 8 shows that convergence of the energy differences and gradients starts at an energy cutoff of 400 eV and explains the need for an energy cutoff of 600 eV in some of the studied systems. Figure S.6 in Supporting Information shows the convergence of the gradient as function of the plane-wave energy cutoff for a larger number of atoms. In general, it can be stated that obtaining a well-conditioned Hessian requires that the value of the plane-wave energy cutoff is set large enough to ensure that energy differences and forces have converged and that an energy cutoff of 400 eV is on the edge of what is required to calculate reliable adsorption entropies in extended zeolite systems.

Also, other extended catalytic systems than zeolites may benefit from this study. As a general guideline, we propose to check the convergence of the energy differences and forces as function of the plane-wave energy cutoff (via some single point calculations) in order to estimate the minimum energy cutoff needed for a particular system, before effectively running the Hessian calculations in VASP. Another option is to follow a similar methodology as presented here for evaluating and comparing FHVA and (various) PHVA results using TAMkin.<sup>37,38</sup>

## 5. CONCLUSIONS

Physisorption and chemisorption of *n*-octane and isobutene complexes in H-ZSM-22 and H-FAU have been studied using periodic DFT calculations. A computationally efficient procedure for performing normal-mode analysis in extended zeolite systems is presented. Physisorption and chemisorption entropies have been calculated from FHVA and various PHVA schemes. All PHVA evaluations can be performed using the TAMkin program, based on the FHVA Hessian without any additional computational cost. The agreement between FHVA and PHVA results is satisfactory, as differences in the calculated physisorption and chemisorption entropies do not exceed  $10 \text{ J mol}^{-1} \text{ K}^{-1}$  provided that stricter convergence criteria for optimization are used, especially for loosely bonded complexes in zeolites. Hence, PHVA provides an attractive alternative for the computationally demanding FHVA calculations to obtain reasonably accurate entropies. The reduction of computational cost when performing

a PHVA instead of a FHVA is significant and amounts to 1 order of magnitude for the systems in this study.

An unambiguous method is presented for the identification of hydrocarbon rotational and translation modes relative to the zeolite. These modes are needed for the application of the mobile adsorbate method in case of loosely bonded complexes. The vibrational frequencies corresponding to these translational and rotational modes that are replaced by free translational and rotational contributions are easily identified based on a MBH–PHVA calculation using the TAMkin package. Physisorption entropies of n-octane and isobutene in H-ZSM-22 and H-FAU obtained from the mobile adsorbate method are predicted within 10–15 J mol<sup>−1</sup> K<sup>−1</sup> as compared to experimental and simulated data available in literature.

The (MBH–)PHVA procedure presented in this work is directly applicable to calculate activation entropies and reaction entropies in extended zeolite systems. The procedure also provides a more efficient methodology for normal vibrational analysis in other extended (catalytic) systems.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Discussion of the loosely bonded n-octane and *t*-butyl carbenium ion complexes in H-FAU, for which unwanted imaginary frequencies are found. Values for physisorption and chemisorption enthalpies and entropies are mentioned, and details on the PHVA choices in H-ZSM-22 and H-FAU are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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