

# An ab initio study of adsorption related properties of diatomic molecules in zeolites

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## Abstract

A perturbational approach (M-method) for the calculation of the interaction energies of N<sub>2</sub>, O<sub>2</sub>, Ar and CO in zeolite cavities is presented. The calculation method is compared with the ‘molecule in point charge environment’ calculation and a full ab initio calculation tested along an axis connecting the center of the cavity with a site II cation. The Henry constants, heats of adsorption and separation constants for N<sub>2</sub>, O<sub>2</sub> and Ar in a NaY zeolite are obtained using the ‘molecule in point charge environment’ method and the present approximation. Different grid sizes were considered depending on the distance between adsorbing system and cation. A promising result, in particular for the separation constants, was found using the Van der Waals and ionic radii for the grid delimitation and the M-method calculated on the B3LYP/6-31G\* level. CO was added as a final test system with lower symmetry. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In the second part of this century, zeolites have revealed their outstanding industrial importance [1–3]. They are used as catalysts, adsorbents, ion exchangers, etc. applications emerging from their particular structure. Zeolites are classified within the three-dimensional aluminosilicates in contrast with clays, which have only a two-dimensional lattice. The three-dimensional structure is built up by tetrahedral silicon and aluminum inter-connected by corner oxygens. In the zeolite lattice, cages and channels are

present in which water and exchangeable cations can be adsorbed. An important feature of those cavities is their uniform size, which can be considered as a sieve with molecular dimensions. The substitution of a silicon atom by an aluminum atom, introduces a net negative charge which has to be compensated by a cation. This cation can be of different nature: a cation of group I, II and in synthetic ones even a transition metal. When a proton is used as a counter ion, these protons form bridging hydroxyls or at defect sites terminal hydroxyls. The zeolite then becomes an ideal catalyst due to its Brønsted acidity [4,5]. This property is used in petroleum refinement and the production of petrochemicals. The adsorbed cations other than H<sup>+</sup> are not part of the framework but are situated inside the cavities; these cations play an important role in the adsorption capacity of zeolites, which is used in separation and purification techniques.

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Both properties, acidity (catalytic activity) [6–8] and adsorption (separation capacity) [9–11] have been studied extensively at the molecular level in the past, to which our group contributed from the eighties on [12–17]. Many theoretical calculations have been performed but a link to macroscopic, thermodynamic properties is not trivial. In the case of catalytic properties, a link to thermodynamic quantities such as reaction enthalpies, etc. is relatively straightforward, in the case of adsorption however, one is facing the evaluation of the Henry constant, which is not trivial at all. Until now, the phenomenon has mainly been described using modeling [18], involving adjustable parameters in potentials [19–21]. In contrast with parametrized methods an ab initio calculation can provide results for not yet or less studied structures and should be the reference method if one is not limited by the computational power available.

The linear relationship between gas or fluid phase and adsorbed phase concentrations is commonly referred to as Henry's law, the proportionality factor or equilibrium constant being called the Henry constant. To predict a Henry constant one has to evaluate the interaction energy between the adsorbing molecule and the zeolite at each point in the zeolite, which is a very intensive computational task, depending on the calculation level and the number of points considered. An interaction energy calculation method is needed and since the calculation power is a limiting factor, a full non-empirical ab initio calculation is still a too lengthy procedure at the moment.

In this work we will discuss an approximation for the interaction energy and look for a final non-empirical recipe for the calculation of the Henry constant of diatomic molecules in faujasite type zeolites. Recently, the first ab initio quantum chemical calculations in a point charge environment have been applied to study the adsorption of O<sub>2</sub> and N<sub>2</sub> in the large cavities of a faujasite [22,23], as well as the influence of the extra framework cations on the adsorption of N<sub>2</sub> and CO [24]. However, showing still the inconvenience to be very time consuming a new method for calculating interaction energies presented by us might cope with that problem. First, a new calculation method for the interaction energies will be derived followed by a thorough investigation of the strategy. The quality of the interaction energies calculated at different levels will be checked and used in

the calculation of Henry constants. Finally, a strategy for obtaining a Henry constant and its derived quantities is considered. The results are reported for N<sub>2</sub>, O<sub>2</sub> and Ar in interaction with a NaY faujasite type zeolite. A final test on a system with lower symmetry (CO) is included.

## 2. Theory and computational details

In order to study the adsorption process in zeolites, one has to quantify it first. This is taken care of by the calculation of the Henry constant of the adsorbing system in the considered zeolite. From this constant, properties mentioned above such as isosteric heats of adsorption, separation constants, etc. are calculated. From statistical mechanics,  $K$  can be written as a ratio of the partition functions of the free and adsorbed gas [18,25], neglecting vibrational corrections upon adsorption and applying the ideal gas law for the non-adsorbed gas. The Henry constant ( $K$ ) is given by

$$K = \frac{BI}{aRT} \quad (1)$$

where  $B$  is the number of cavities in which the adsorption can take place per mass zeolite,  $R$  the ideal gas constant and  $T$  the absolute temperature. The factor  $a$  is equal to 1 in the case of a monoatomic gas,  $4\pi$  for a linear molecule and  $8\pi^2$  for a non-linear molecule [26].  $I$  is the configuration integral.

The variation of  $\ln K$  with the temperature gives the van't Hoff equation

$$\frac{\partial \ln K}{\partial(1/T)} = -\frac{\Delta H^0}{R} \quad (2)$$

where  $\Delta H^0$  is the isosteric heat of adsorption.

For an atom, the configuration integral  $I$  can be written as

$$I = \int e^{-E(r)/RT} d\underline{r} \quad (3)$$

and for a molecule as

$$I = \int e^{-E(r,\phi)/RT} d\underline{r} d\underline{\phi} \quad (4)$$

where  $E$  represents the interaction energy between the adsorbed atom or molecule and the zeolite cage when

the center of gravity of the atom or molecule is at position  $\underline{r}$  and the molecular orientation is gathered in vector  $\underline{\phi}$ . In the special case of an atom the configuration integral was approximated as follows:

$$I \approx \sum_i e^{-E_{r_i}/RT} \Delta V_i \quad (5)$$

with  $\Delta V_i$  is the elementary volume around position  $i$  in the cage for which a value of  $0.125 \text{ \AA}^3$  was found to yield the best performance from a quality/cost ratio point of view [23]. For a linear molecule, the rotational integration was simplified by calculating the interaction energy of the molecule aligned along the three different Cartesian axis and multiplying each contribution  $\exp(-E_\alpha/RT)$  ( $\alpha = x, y, z$ ) by  $4\pi/3$ .

$$I \approx \frac{4\pi}{3} \sum_i (e^{-E_{x_i}/RT} + e^{-E_{y_i}/RT} + e^{-E_{z_i}/RT}) \Delta V_i \quad (6)$$

In the cage, a cubic grid of points was constructed and the points were selected on the basis of the distance between an atom of the molecule and the zeolite.

The point of interest is the way interaction energies are evaluated since they are the only ‘unknown’ in these equations. This can be done at different levels of calculation or approximation. Firstly, one could think to calculate the interaction energy ab initio, which is feasible for the interaction of small molecular systems, but unrealistic, at the moment, if thousands of ab initio calculations should be performed in order to obtain a Henry constant. Such kind of calculations were performed on a few points inside a zeolite cavity and will be discussed in this paper.

Secondly, one could simulate the cavity with point charges, obtained from an ab initio calculation. This procedure is known as the ‘molecule in point charge field method’ as often used in molecular crystals [27], which will be abbreviated as Q-method. The interaction energy will then be evaluated for the system in interaction with a point charge field mimicking the zeolite cavity. The point charges are obtained using the ChelpG formalism [28] calculated at the STO-3G level, in an other work those point charges were calculated with a 3-21G basis set and compared with the Mulliken charges [24]. The Q-method is a lot faster than a fully ab initio study but still very time consuming when a configuration integral has to be calculated. To accelerate the calculation we propose a Density

Functional Theory (DFT) based approach [29] for the evaluation of interaction energies. Density Functional Theory [30] has been the framework for the introduction of many chemical concepts used in the description of isolated and interacting systems. These concepts originate from differentiation of the electronic energy  $E$  for the ground state of an atomic or molecular system with respect to properties, e.g. the number of electrons  $N$  or the external (i.e. due to the nuclei) potential  $v(\underline{r})$ .

The total differential of the energy,  $E[N, v(\underline{r})]$  can thus be written as

$$dE[N, v(\underline{r})] = \left( \frac{\partial E}{\partial N} \right)_{v(\underline{r})} dN + \int \left[ \frac{\delta E}{\delta v(\underline{r})} \right]_N \delta v(\underline{r}) d\underline{r} + \Delta V_{NN} \quad (7)$$

where the first term represents the energy change due to charge transfer, the second term the energy change due to the change in external potential and the last term the change in nuclear–nuclear repulsion energy.

Using the identities [30]

$$\mu = \left( \frac{\partial E}{\partial N} \right)_v \quad \text{and} \quad \rho(\underline{r}) = \left[ \frac{\delta E}{\delta v(\underline{r})} \right]_N \quad (8)$$

this expression can be rewritten as

$$dE[N, v(\underline{r})] = \mu dN + \int \rho(\underline{r}) \delta v(\underline{r}) d\underline{r} + \Delta V_{NN} \quad (9)$$

As mentioned in the introduction our main concern is the calculation of  $dE$  for an adsorption process. This type of process implies  $dN$  to be zero as there is no charge transfer which is also the case in the previous studies of solvent effects [31] and fullerene endohedral complexes [32]. Eq. (5) thus can be written for an adsorption process as

$$dE = \int \rho(\underline{r}) \delta v(\underline{r}) d\underline{r} + \Delta V_{NN} \quad (10)$$

This equation shows the change in energy as a function of the perturbation in the external potential  $v(\underline{r})$ , a perturbation due to the presence of the partner in the adsorption process (i.e. the zeolite cage that is surrounding the adsorbed molecule). Applying standard first-order perturbation theory to the electron

density yields

$$\rho(\underline{r}) = \rho_0(\underline{r}) + \int \left[ \frac{\delta\rho(\underline{r})}{\delta v(\underline{r}')} \right]_N \delta v(\underline{r}') d\underline{r}' \quad (11)$$

where  $\rho_0(\underline{r})$  is the unperturbed electron density of the molecule. Introducing the linear response function  $\omega(\underline{r}, \underline{r}')$  [30], this equation becomes

$$\rho(\underline{r}) = \rho_0(\underline{r}) + \int \omega(\underline{r}, \underline{r}') \delta v(\underline{r}') d\underline{r}' \quad (12)$$

Introduction of Eq. (12) into (10) yields

$$\begin{aligned} dE &= \int \rho_0(\underline{r}) \delta v(\underline{r}) d\underline{r} + \Delta V_{NN} \\ &+ \iint \omega(\underline{r}, \underline{r}') \delta v(\underline{r}') \delta v(\underline{r}) d\underline{r} d\underline{r}' \\ &= dE_1 + dE_2 \end{aligned} \quad (13)$$

The first term,  $dE_1$ , in this equation describes the electrostatic interaction between two molecules in terms of the non-perturbed electron density of the adsorbed molecule and the change in the external potential for this system due to the presence of the adsorbing molecule (the zeolite cage in our case).

The second term is a correction term arising from the fact that the electron density of the adsorbed molecule changes upon introduction of the zeolite cage. Both terms are the counterparts of the well known electrostatic and polarization terms arising via a more conventional perturbational approach [33,34].

The external potential due to the presence of the zeolite cage can be approximated by means of a number of point charges,  $q_i$ , at positions  $\underline{R}_i$

$$\delta v(\underline{r}) \approx - \sum_i \frac{q_i}{|\underline{r} - \underline{R}_i|} \quad (14)$$

So, the first two terms in (13) can be written as

$$\Delta E_1 = \sum_i q_i V(\underline{R}_i) \quad (15)$$

where  $q_i$  is the charge of the cage atom  $i$  and  $V(\underline{R}_i)$  the classical molecular electrostatic potential (MEP) of the adsorbed molecule evaluated at position  $\underline{R}_i$  of the cage atom  $i$ . As the result is equivalent to the electrostatic energy evaluation, this method will be referred to as the molecular electrostatic potential or multipole moment approximation (M). Via the multipole expansion

one can approximate the molecular electrostatic potential calculated in the M-method (15) via the dipole and quadrupole interactions. The energy of a molecule in an external uniform electric field  $\underline{F}$ , provided that the origin is located at the center-of-mass, can be written as a power series in  $\underline{F}$ .

$$\begin{aligned} E(\underline{F}) &= E - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma \\ &- \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta - \dots \end{aligned} \quad (16)$$

where  $\mu$  is the dipole moment,  $\alpha$  the polarizability,  $\beta$  the hyper-polarizability and  $\gamma$  the second hyper-polarizability. When the external field  $\underline{F}$  is non-uniform, additional distortions are induced. The energy may then be expressed as a power series in  $F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, \dots$

$$\begin{aligned} E(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, \dots) \\ &= E - \mu_\alpha F_\alpha - \frac{1}{3} \Theta_{\alpha\beta} F_{\alpha\beta} - \frac{1}{15} \Omega_{\alpha\beta\gamma} F_{\alpha\beta\gamma} \\ &- \frac{1}{105} \Phi_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta} - \frac{1}{2} \alpha_\alpha F_\alpha F_\beta \\ &- \frac{1}{6} C_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} - \dots \end{aligned} \quad (17)$$

here is  $F_\alpha, F_{\alpha\beta}$  the field, field gradient, etc. at the origin,  $\mu, \Theta, \Omega$  and  $\Phi$  are the dipole, quadrupole, octupole and hexadecapole moment tensors of the free molecule,  $\beta, C$ , respectively, are the dipole and quadrupole polarizabilities. The Greek subscript denote the Cartesian components ( $x, y$  and  $z$ ) and a repeated subscript implies summation over the latter.

### 3. Results and discussion

#### 3.1. Isolated molecule properties

The geometry optimizations for the sorbates and the interaction energy calculations were performed using the HF-method in combination with the B3LYP [35–37] functional (Table 1). The latter has proven to give accurate results in charge distributions and derived properties [38–40] in combination with a 6-31G\* basis set [41]. The BSSE error (for an overview see [42]) was treated with the counterpoise correction [43].

For  $N_2, O_2$  ( $D_{\infty h}$  symmetry) the quadrupole moment plays the most important role. CO has only  $C_{\infty v}$  symmetry but has a very small dipole moment. So, the

Table 1  
Optimized distances for X<sub>2</sub>, the X...Na<sup>+</sup> complex (values in Å) and the number of grid points used in the calculation of the Henry constant

	Method	HF/STO-3G	HF/6-31G*	B3LYP/STO-3G	B3LYP/6-31G*
N <sub>2</sub>	D <sub>eq</sub> (X <sub>2</sub> )	1.1339	1.0784	1.1807	1.1055
	D <sub>eq</sub> (X...Na <sup>+</sup> )		2.5012		2.4466
	Number of points		3101		3143
O <sub>2</sub>	D <sub>eq</sub> (X <sub>2</sub> )	1.2172	1.1678	1.2853	1.2145
	D <sub>eq</sub> (X...Na <sup>+</sup> )		2.3846		2.3368
	Number of points		3194		3255
Ar	D <sub>eq</sub> (X <sub>2</sub> )				
	D <sub>eq</sub> (X...Na <sup>+</sup> )		2.9312		2.8121
	Number of points		3109		3242
CO	D <sub>eq</sub>				1.1692

quadrupole moment of these four systems is expected to play the most important role in the interaction with the cations. From Table 2 it can be noticed that the B3LYP/6-31G\* quadrupole moments are closer to the experimental values than in the case of HF/6-31G\*, except for nitrogen which can be considered as fortuitous. The larger deviation from the experimental value of oxygen can be attributed to the uncertainty in the experimental value. The quadrupole moment of oxygen was recently considered to be in need of reevaluation by Dickson and Becke [48], a conclusion drawn also by our group in a recent study on the high level DFT-calculations of dipole and quadrupole moments [49]. For the B3LYP-calculation, about 6% deviation for the quadrupole moments is found (see Table 2).

The cluster (see Fig. 1) was chosen to represent a faujasite Y zeolite cage, using hydroxyl groups as terminators and showing a Si/Al ratio of 3, with for-

mula Na<sub>16</sub>Si<sub>36</sub>Al<sub>12</sub>O<sub>120</sub>H<sub>48</sub>. Four of the sixteen Na<sup>+</sup> cations are localized in a site II with a tetrahedral orientation towards the center of the large cavity, the rest of the cations are localized in a site I position.

All calculations have been carried out using the Gaussian 94 [50] package running on the Cray J916/8-1024 at the Brussels Free University Computer Center.

### 3.2. The calculation and the study of the interaction energies

As mentioned above the interaction energy is investigated in a NaY-cage. This was done by calculating the energy along a line, hereafter referred as the X-axis, connecting the center of the cavity and one of the Na<sub>II</sub><sup>+</sup> cations (Fig. 1). The results given in Tables 3 and 4 show the interaction energy from ab initio calculations (AI) (i.e. fully ab initio and BSSE corrected), from the 'molecule in point charge field method' (Q) and from the molecular electrostatic potential approximation (M), for nitrogen and oxygen with the inter nuclear axis along the X-axis (see Figs. 2 and 3). The approximated interaction energies were also calculated with the molecule oriented perpendicular to the X-axis<sup>2</sup> (see Figs. 4 and 5).

In the approximate schemes, (Q and M) calculations were done using the HF and the B3LYP-method both in combination with the STO-3G basis set as well as the 6-31G\* basis set, so that the influence of the basis set could be studied as well (see Tables 3 and 4).

Table 2  
Calculated and experimental dipole moments ( $\mu$ ) and (traceless) quadrupole moments ( $\Theta_{\alpha\beta}$ ) for the different systems considered, calculated relative to the center of mass<sup>a</sup>

		B3LYP/6-31G*	HF/6-31G*	EXP
N <sub>2</sub>	$\Theta_{xx} = \Theta_{yy}$	0.5792	0.5533	
	$\Theta_{zz}$	-1.1584	-1.1065	-1.09 [44]
O <sub>2</sub>	$\Theta_{xx} = \Theta_{yy}$	0.17055	0.2026	
	$\Theta_{zz}$	-0.3411	-0.4053	0.25 [45]
				-0.299 [46]
CO	$\mu$	0.0236	-0.1037	0.0433 [47]
	$\Theta_{xx} = \Theta_{yy}$	0.7689	0.8146	
	$\Theta_{zz}$	-1.5378	-1.6294	-1.44 [47]

<sup>a</sup> Orientation with the axis of highest symmetry coinciding with the z-axis (values in a.u.).

<sup>2</sup> The Y and Z-axis are perpendicular to each other and arbitrarily chosen.

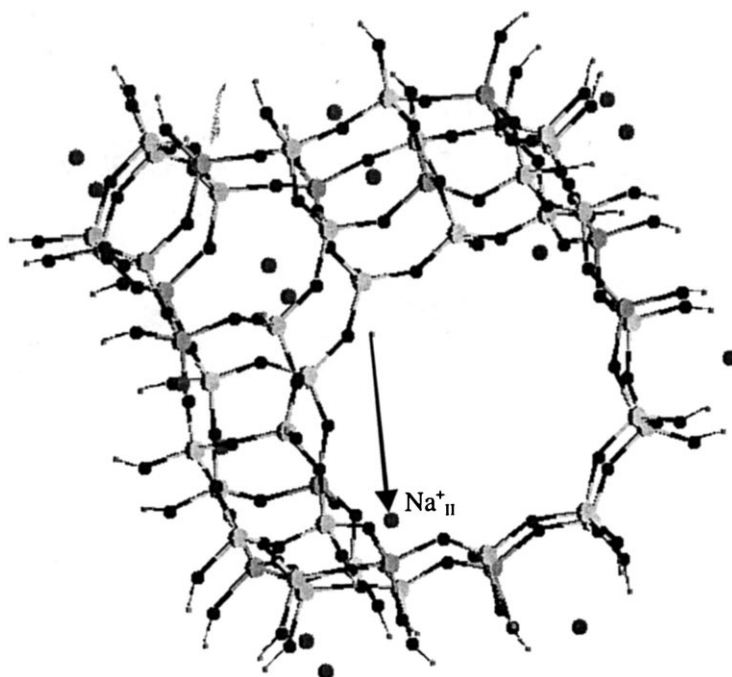


Fig. 1. Model of the faujasite cage used in the calculations, indicating the axis used in the “one-dimensional” case.

Table 3

Interaction energies calculated for  $N_2$  in a faujasite cage on a straight line starting in the center of the cavity into the direction of a  $Na_{II}^{+a}$

$N_2$ $r$ (Å)	HF/STO-3G				HF/6-31G*		B3LYP/STO-3G		B3LYP/6-31G*	
	AI <sup>b</sup>	AI <sup>b,c</sup>	Q <sup>d</sup>	M <sup>e</sup>	Q <sup>d</sup>	M <sup>e</sup>	Q <sup>d</sup>	M <sup>e</sup>	Q <sup>d</sup>	M <sup>e</sup>
0	-0.192	-0.188	0.000	-0.188	0.000	-0.134	0.000	-0.188	0.000	-0.130
0.25	-1.561	-1.552	-1.314	-1.494	-0.782	-0.900	-1.180	-1.335	-0.778	-0.971
0.50	-3.096	-3.067	-2.774	-2.979	-1.678	-1.745	-2.494	-2.657	-1.732	-1.820
0.75	-4.879	-4.786	-4.422	-4.577	-2.720	-2.736	-3.979	-4.142	-2.837	-2.828
1.00	-7.075	-6.807	-6.326	-6.460	-3.979	-3.862	-5.707	-5.816	-4.142	-4.012
1.25	-9.586	-9.305	-8.606	-8.623	-5.573	-5.180	-7.778	-7.766	-5.791	-5.322
1.50	-14.217	-12.573	-11.443	-11.305	-7.686	-6.795	-10.372	-10.188	-7.975	-7.017
1.75	-20.472	-16.991	-15.117	-14.657	-10.636	-8.828	-13.749	-13.213	-11.008	-9.104
2.00	-29.259	-22.727	-20.071	-19.066	-14.941	-11.527	-18.338	-17.184	-15.447	-11.837
2.25	-39.351	-28.577	-27.041	-25.025	-21.543	-15.175	-24.840	-22.585	-22.255	-15.539
2.50	-44.334	-28.752	-37.267	-33.468	-32.121	-20.313	-34.459	-30.317	-33.171	-20.728
2.75	-24.815	-4.979	-52.890	-45.928	-49.543	-27.372	-49.275	-41.593	-51.200	-27.761
3.00	69.936	92.588	-77.408	-64.505	-77.772	-36.133	-72.664	-58.354	-80.404	-36.325

<sup>a</sup> All values are in kJ/mol.

<sup>b</sup> Ab initio calculation.

<sup>c</sup> ‘BSSE corrected’.

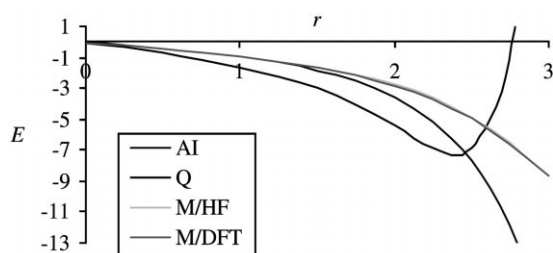
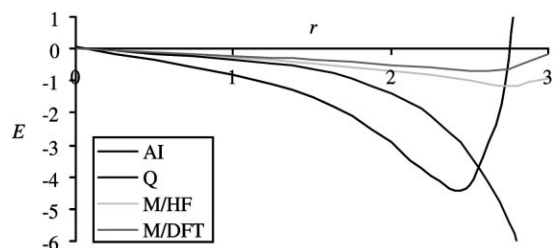
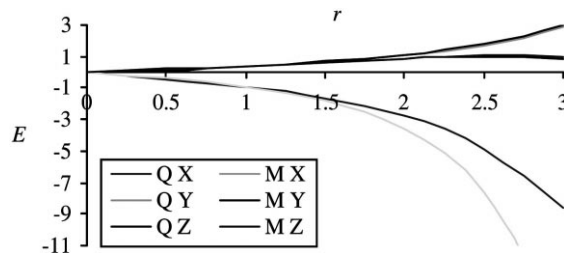
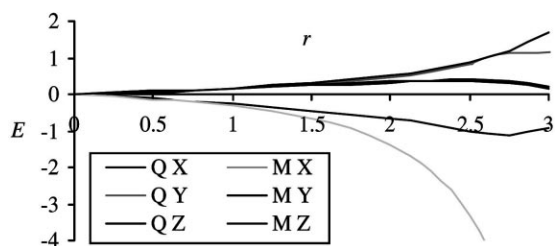
<sup>d</sup> ‘Molecule in point charge environment’ method.

<sup>e</sup> Calculated using formula (5) (M-method).

Table 4

Interaction energies calculated for O<sub>2</sub> in a faujasite cage on a straight line starting in the center of the cavity into the direction of a Na<sub>II</sub><sup>+</sup><sup>a</sup>

O <sub>2</sub> <i>r</i> (Å)	HF/STO-3G				HF/6-31G*		B3LYP/STO-3G		B3LYP/6-31G*	
	AI <sup>b</sup>	AI <sup>b,c</sup>	Q <sup>d</sup>	M <sup>e</sup>	Q <sup>d</sup>	M <sup>e</sup>	Q <sup>d</sup>	M <sup>e</sup>	Q <sup>d</sup>	M <sup>e</sup>
0	0.280	0.285	0.000	-0.013	0.000	0.079	0.000	0.004	0.000	0.071
0.25	-0.720	-0.711	-0.632	-0.611	-0.280	-0.222	-0.481	-0.406	-0.151	-0.142
0.50	-1.498	-1.485	-1.322	-1.310	-0.586	-0.494	-0.971	-0.908	-0.197	-0.372
0.75	-2.397	-2.347	-2.092	-2.079	-0.937	-0.812	-1.515	-1.448	-0.870	-0.623
1.00	-3.515	-3.356	-2.975	-2.891	-1.368	-1.121	-2.142	-1.975	-1.238	-0.866
1.25	-5.075	-4.611	-4.033	-3.887	-1.933	-1.481	-2.904	-2.669	-1.732	-1.138
1.50	-7.556	-4.816	-5.364	-5.033	-2.766	-1.883	-3.874	-3.423	-2.439	-1.431
1.75	-11.828	-8.732	-7.109	-6.439	-3.966	-2.339	-5.167	-4.389	-3.510	-1.770
2.00	-19.066	-12.247	-9.573	-8.217	-5.837	-2.853	-6.979	-5.561	-5.201	-2.142
2.25	-29.727	-16.468	-13.046	-10.565	-8.845	-3.502	-9.623	-7.033	-7.983	-2.489
2.50	-40.183	-17.661	-18.221	-13.761	-13.883	-4.188	-13.657	-9.088	-12.732	-2.849
2.75	-34.744	-1.205	-26.338	-18.230	-22.673	-4.736	-20.087	-11.816	-21.121	-2.753
3.00	33.489	78.308	-39.388	-24.556	-37.790	-3.908	-30.727	-15.280	-35.886	-0.770

<sup>a</sup> All values are in kJ/mol.<sup>b</sup> Ab initio calculation.<sup>c</sup> 'BSSE corrected'.<sup>d</sup> 'Molecule in point charge environment' method.<sup>e</sup> Calculated using formula (5) (M-method).Fig. 2. Interaction energy *E* of nitrogen calculated at four different levels (AI, Q/HF/6-31G\*, M/HF/6-31G\* and M/B3LYP/6-31G\*) in a faujasite cage on a straight line from the center of the cage into the direction of a Na<sub>II</sub><sup>+</sup> cation (distance *r* denoted in Å). (M curves indistinguishable).Fig. 3. Interaction energy of oxygen calculated at four different levels (AI, Q/HF/6-31G\*, M/HF/6-31G\* and M/B3LYP/6-31G\*) in a faujasite cage on a straight line from the center of the cage into the direction of a Na<sub>II</sub><sup>+</sup> cation (distance *r* denoted in Å).Fig. 4. Q and M interaction energies of nitrogen calculated at the HF/6-31G\* level plotted for the three orientations (X,Y,Z) in a faujasite cage on a straight line from the center of the cage into the direction of a Na<sub>II</sub><sup>+</sup> cation (distance *r* denoted in Å). (repulsive curves QY/MY and QZ/MZ indistinguishable).Fig. 5. Q and M interaction energies of oxygen calculated at the HF/6-31G\* level plotted for the three orientations (X,Y,Z) in a faujasite cage on a straight line from the center of the cage into the direction of a Na<sub>II</sub><sup>+</sup> cation (distance *r* denoted in Å). (repulsive curves QY/MY and QZ/MZ quasi indistinguishable).

The third system considered in our study, argon, is taken as test system because of the more simple calculation due to its spherical symmetry. The electron density and the resulting molecular electrostatic potential ( $V(r)$ ) has been studied for atoms by Politzer, Sen and co-workers [51,52]. Since no minimum is found in  $V(r)$ , the interaction energy calculated with the M-method (5) or with the Q-method is attractive in the neighborhood of negative charges, in our case the oxygen atoms. Ab initio, we find that the main interaction in the cage occurs with the cations, in contrast with the approximated methods (Q- and M-method) where repulsion is noticed.

The global performance of the approximations as a function of the position in the cage was compared (Table 5). In the case of nitrogen the M approximation shows a better fit with the AI curve until 1.25 Å, both approximations performing very well until 1.50 Å. At shorter distance the approximations encounter more difficulties to reproduce the AI potential, in this region the Q-calculation performs the best. This was expected since the Q-calculations are less approximate. For oxygen the Q-calculations perform the best over all distances unless close to the cage (i.e.  $r > 2.50$  Å), M reproduces the potential quite good until 1.50 Å from the center. The difference between both approximations is less for nitrogen.

So, one can conclude that in general Q-calculations perform the best and that the difference be-

tween both approximations is less pronounced for nitrogen.

### 3.3. The calculation of Henry constants

The determination of the grid points on which the interaction energies should be calculated is the first step in the calculation of a Henry constant. When the interaction energies are calculated, the Henry constant can be obtained from formula (1). The Henry constants are calculated with the Q-method on the HF/6-31G\* level and with the M-method for nitrogen, oxygen and argon (Table 6). In view of the nature of the potential used, a smallest distance between the adsorbing molecule and the cage has to be determined for the selection of the grid points (Table 1). At smaller distance the potential is considered to be repulsive leading to large positive energy values in (3,4), which upon insertion in the exponential yield small contributions to the integration.

The distance between an atom of the adsorbent and the sodium cation is used as a criterion for the grid point selection. In the first series of Henry constants  $\{D_{eq}\}$  all points which have a distance between the cation and the atom smaller than  $D_{eq}(Na^+ \cdots X)$  are discarded (this distance was obtained by optimizing the complex in the gas phase). The HF-method and the B3LYP functional were used to obtain the optimized geometry for the sorbates (see Table 1) and the

Table 5

Differences between AI calculated interaction energies for N<sub>2</sub> and O<sub>2</sub> and both approximations, all calculated along a line connecting the center of the cavity with a Na<sup>+</sup> cation on the HF/STO-3G level<sup>a</sup>

$r$ (Å)	N <sub>2</sub>			O <sub>2</sub>		
	AI-Q	AI-M	M-Q	AI-Q	AI-M	M-Q
0	-0.188	0.000	-0.188	0.285	0.297	-0.013
0.25	-0.238	-0.059	-0.180	-0.079	-0.100	0.021
0.50	-0.293	-0.088	-0.205	-0.163	-0.176	0.013
0.75	-0.364	-0.209	-0.155	-0.255	-0.268	0.013
1.00	-0.481	-0.347	-0.134	-0.381	-0.464	0.084
1.25	-0.699	-0.682	-0.017	-0.577	-0.724	0.146
1.50	-1.130	-1.268	0.138	0.548	0.218	0.331
1.75	-1.874	-2.335	0.460	-1.623	-2.293	0.669
2.00	-2.657	-3.661	1.004	-2.674	-4.029	1.356
2.25	-1.536	-3.552	2.017	-3.423	-5.904	2.481
2.50	8.514	4.715	3.799	0.561	-3.899	4.460
2.75	47.911	40.949	6.962	25.133	17.025	8.109
3.00	169.996	157.092	12.903	117.696	102.864	14.832

<sup>a</sup> Values in kJ/mol.



Table 6

Calculated Henry constants ( $K$ ), isosteric heats of adsorption ( $\Delta H^0$ ) and distances ( $r$ ) between system and cage atoms, determining the grid size<sup>a</sup>

	N <sub>2</sub>				O <sub>2</sub>				Ar				CO			
	Q/HF/ 6-31G*	M/HF/ 6-31G*	M/B3LYP/ 6-31G*	EXP <sup>b</sup> [24]	Q/HF/ 6-31G*	M/HF/ 6-31G*	M/B3LYP/ 6-31G*	EXP <sup>b</sup> [24]	Q/HF/ 6-31G*	M/HF/ 6-31G*	M/B3LYP/ 6-31G*	EXP <sup>b</sup> [24]	Q/HF/ 6-31G*	M/HF/ 6-31G*	M/B3LYP/ 6-31G*	EXP <sup>b</sup> [24]
$D_{\text{eq}}^c$																
$r$	2.501	2.501	2.447		2.385	2.385	2.337		2.931	2.931	2.812					
$K$	82.932	2.506	2.843		2.367	0.680	0.671		0.885	0.600	0.626					
$\Delta H^0$	-26.323	-11.443	-12.014		-9.027	-2.995	-2.831		-3.525	-2.453	-2.451					
$D_{\text{eq}}(\text{Al})^d$																
$r$	2.926	2.926	2.926		2.884	2.884	2.884		2.491	2.491	2.491					
$K$	2.233	0.763	2.051		0.812	0.464	0.454									
$\Delta H^0$	-10.2	-5.548	-5.694		-4.588	-2.749	-2.658									
$D(\text{VdW})^e$																
$r$	2.71	2.71	2.71		2.66	2.66	2.66		3.06	3.06	3.06			2.66/2.86		
$K$	2.762	1.082	1.54	31.4	1.212	0.553	0.535	15.4	0.81	0.546	0.546	14.8		3.65		85
$\Delta H^0$	-14.686	-6.761	-7.166	-14	-5.925	-2.843	-2.718	-9.4	-3.392	-2.45	-2.45	-9		-14.59		-20

<sup>a</sup>  $K$  in  $10^{-7}$  mol/kg Pa,  $\Delta H^0$  in kJ/mol and  $r$  in Å.<sup>b</sup> Si/Al-ratio of the NaY zeolite is equal to 2.55.<sup>c</sup>  $D_{\text{eq}}(\text{X}\cdots\text{Na}^+)$  from optimization between adsorbed system and  $\text{Na}^+$  in gas phase.<sup>d</sup>  $D_{\text{eq}}(\text{X}\cdots\text{Na}^+)$  from fitting the ab initio potential in the faujasite cage.<sup>e</sup>  $D_{\text{eq}}(\text{X}\cdots\text{Na}^+)$  obtained by adding Van der Waals radii of X and ionic radii of  $\text{Na}^+$ .

Table 7  
Calculated separation constants<sup>a</sup>

	Q/HF/6-31G*			M/HF/6-31G*			M/B3LYP/6-31G*			EXP [24]
	$D_{\text{eq}}$	$D_{\text{eq}}(\text{AI})$	$D(\text{VdW})$	$D_{\text{eq}}$	$D_{\text{eq}}(\text{AI})$	$D(\text{VdW})$	$D_{\text{eq}}$	$D_{\text{eq}}(\text{AI})$	$D(\text{VdW})$	
$\alpha_1$	35.04	2.75	4.75	3.69	1.65	1.96	4.24	1.72	2.88	2.04
$\alpha_2$	93.71		7.11	4.18		1.98	4.54		2.82	2.12
$\alpha_3$	2.67		1.5	1.13		1.01	1.07		0.98	1.04
$\alpha_4$									2.37	2.7
$\alpha_5$									6.82	5.52
$\alpha_6$									6.68	5.74

<sup>a</sup>  $\alpha_1 = K(\text{N}_2)/K(\text{O}_2)$ ,  $\alpha_2 = K(\text{N}_2)/K(\text{Ar})$ ,  $\alpha_3 = K(\text{O}_2)/K(\text{Ar})$ ,  $\alpha_4 = K(\text{CO})/K(\text{N}_2)$ ,  $\alpha_5 = K(\text{CO})/K(\text{O}_2)$ ,  $\alpha_6 = K(\text{CO})/K(\text{Ar})$ .

reported results for the energy calculations (Tables 3 and 4). An interaction energy calculation at more than 3000 points is necessary, indicating that even modest STO-3G-calculations are prohibitive to calculate a Henry constant non-empirically, certainly if comparative studies are undertaken. The calculation time can be pulled down with a factor 1000 and even more when the M-method is used.

The separation constants are surprisingly high, especially when calculated with the Q-method, but show the right trend (Table 7). The very large Henry constant for nitrogen and the extremely low Henry constant for argon are the reason for these high separation constants. Since the experimental Henry constants are determined within 10% [53], one should keep in mind that both separation constants  $\alpha_1$  and  $\alpha_2$  can be seen as equal. The correct description of free space in the cage is one of the main problems. The potential in the cage was analyzed, because a full optimization of a molecule in the cage is not feasible. The grid points were selected on distances originating from optimizations in the gas phase and not in the zeolite. If the 'correct' equilibrium distance is smaller than the one used, one passes the minimum in the potential and enters in the repulsive part. Unfortunately, our models do not represent this part (see Figs. 2 and 3). Thus, one adds extra attraction energy when going beyond the equilibrium distance which is not realistic. By calculating the configuration integral (3 and 4) in which an exponential is taken of an exponential function (i.e. the approximation of the potential) this effect is accentuated, which is more important for nitrogen than for oxygen (see Figs. 2 and 3). This effect is not as big in the M-calculations because of the less pronounced decrease of the interaction energy when approaching

the Na-cation. From this, one can conclude that with this selection criterion of grid points the M-method performs the best.

In the second series  $\{D_{\text{eq}}(\text{AI})\}$  the equilibrium distance between both systems is found by fitting the potential in the faujasite cage. The potential in the cage along the X-axis, (cf. study of the interaction energies), was obtained by plotting the interaction energies as a function of the distance (Figs. 2 and 3). The equilibrium distance and the interaction energy can be found by a best fit of those points; a 4th order polynome was used to fit the curves. So, an ab initio interaction energy is found of  $-44.39$  kJ/mol at  $2.481$  Å (BSSE corrected:  $-29.83$  kJ/mol at  $2.400$  Å) from the center of the cage for nitrogen. For oxygen an interaction energy of  $-41.84$  kJ/mol at  $2.598$  Å (BSSE corrected:  $-17.95$  kJ/mol at  $2.442$  Å) is found. This result gives an equilibrium distance between nitrogen and the sodium cation and oxygen and the sodium cation of  $2.845$  Å (BSSE corrected:  $2.926$  Å) and  $2.728$  Å (BSSE corrected:  $2.884$  Å), respectively. From the ab initio study one could fit the potential to obtain the equilibrium distance and interaction energy between argon and the  $\text{Na}^+$ , which is, BSSE corrected:  $-23.93$  kJ/mol at  $2.491$  Å.

Semi ab initio values for the interaction energy and the equilibrium distances were obtained. Results for the separation constants which are very close to the experimental values especially for the Q-method are found but the trend is not respected. Since no negative region is encountered in atomic electrostatic potentials [51,52] the Henry constant for argon is overestimated and not realistic.

In the third method, the minimum distance between both interacting systems was chosen equal to the sum

of the Van der Waals radii [54] of the interacting system and the ionic radius [55] of the cation, the use of the Van der Waals radii in potential calculations being proposed before by Gadre et al. [56]. For this method we found the right sequence in all methods. This criterion is remarkably good for the M-calculations. A fourth (hetero-nuclear) system (carbon monoxide) whose experimental Henry constant value was unknown at the time we started this investigation was added to be certain we found a good criterion and calculation strategy. Twice as much calculations had to be performed, because of the  $C_{\infty v}$  symmetry of CO, in Eq. (4) two orientations ( $\text{Na}^+\cdots\text{OC}$ : 2.66 Å and  $\text{Na}^+\cdots\text{CO}$ : 2.86 Å) with two different Van der Waals radii had to be considered. From Table 6, one can note also a good correlation between the experimental and calculated Henry constants and separation constants. The  $\Delta H^0$  is underestimated (see Table 6) as was found in previous systems.

The extreme sensitivity of the interaction energy values appearing in the exponent of configuration integral leads to Henry constants with a magnitude of roughly one order too small. As was shown in our former study [22], a difference of one order of magnitude is the result of a uniform difference in interaction energy of only 5.86 kJ/mol (1.4 kcal/mol).

Summarizing these findings the following can be concluded: the semi ab initio equilibrium distance criterion for the grid points works very well for Q-calculation method; however, the Van der Waals radii-based criterion gives good results with the M-method and even better when the energies of interaction are calculated with the HF-method. The better performance of HF-method compared to the B3LYP-method can be considered as fortuitous, B3LYP includes partially electron correlation effects, which HF does not. B3LYP should provide results of higher quality, due to the overall quality of the isolated molecule properties with B3LYP type DFT-calculations [38–40]. The M/B3LYP/6-31G\*-method (the data of the last row of Table 7), with a computation time being reduced by a factor of more than 1000 as compared to the ab initio one, give the most encouraging results, definitely from the ‘quality/cost ratio’ perspective and can be advised as an attractive recipe for further investigations.

The accuracy of the calculation could be increased using a combination of M/B3LYP/6-31G\*-method

and AI-calculations, which can be interesting for more complex systems where the interaction energy is not well approximated. This will give us a better description in the area close to the cations. From Table 5, which is discussed above, we conclude that the M-technique should be used until 2.50 Å from the center of the cavity, the difference between the Q- and M-method being insignificant in the central area of the cavity, and AI-calculations for the remaining region until the cation.

Isosteric heats of adsorption were obtained using the van’t Hoff equation. The expected trend is reproduced nicely, however as was the case for the Henry constants the values are too small in comparison with experiment. This underestimation is ascribed to the way the interaction energies are calculated. In the zeolite cage the interaction energy is underestimated until the equilibrium region, whereas, beyond this region the potential is overestimated in both methods (Q and M) (see Figs. 2 and 3). In order to obtain more realistic interaction energies the method of approximation needs to be refined facing however the possible obligation of introducing adaptable parameters. The further development of parameter free investigations is in progress.

#### 4. Conclusions

A method for the calculation of interaction energies of small molecules in zeolite cavities is presented. The calculation method is based on a DFT-perturbational approach. The first order perturbation term coincides with the pure electrostatic term found in the multipole expansion of the interaction energy. The obtained expression was compared with the commonly used ‘molecule in point charge environment’ method and a full ab initio result. A calculation strategy was set up and refined accelerating the calculation in comparison with the Q-method. The partitioning of the cage depending on the calculation quality of the interaction energy was also discussed. The Henry constants for nitrogen, oxygen and argon in a NaY zeolite were calculated with both approximations (Q and M). The influence of the grid choice was found to be important. The best grid was delimited by the Van der Waals and ionic radii of the adsorbing system and the cation respectively. The best results, from a

‘quality/cost ratio’ point of view, were obtained using the M-method calculated on the B3LYP/6-31G\* level, yielding  $1.54 \times 10^{-7}$ ,  $0.535 \times 10^{-7}$ ,  $0.546 \times 10^{-7}$  and  $3.65 \times 10^{-7}$  mol/kg Pa for nitrogen, oxygen, argon and carbon monoxide, respectively and separation constants of 2.88, 2.82, 1.02, 2.37, 6.82 and 6.68 ( $\alpha_1 = K(\text{N}_2)/K(\text{O}_2)$ ,  $\alpha_2 = K(\text{N}_2)/K(\text{Ar})$ ,  $\alpha_3 = K(\text{O}_2)/K(\text{Ar})$ ,  $\alpha_4 = K(\text{CO})/K(\text{N}_2)$ ,  $\alpha_5 = K(\text{CO})/K(\text{O}_2)$ ,  $\alpha_6 = K(\text{CO})/K(\text{Ar})$ ) which are in very good accordance with the experiment. The corresponding heats of adsorption ( $-7.166$ ,  $-2.718$ ,  $-2.450$  and  $-14.59$  kJ/mol) are systematically too small but show the correct sequence.

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