

Induced Infrared Absorption of Molecular Oxygen Sorbed in Exchanged A Zeolites. 2. Frequency Shift Calculation

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O₂ sorbed in NaA, NaCaA, and CaA exhibits induced infrared bands whose frequencies are differently shifted with respect to the gas phase frequency. In the preceding article, we analyzed the intensity of these bands. The shift depends on the molecule–zeolite interaction, by the variation of the latter with respect to the normal coordinate of the molecule. We have calculated this interaction, to determine the adsorption sites of O₂ in these zeolites. It was shown that the main adsorption site in NaA is in front of the Na_{III} cation. The oxygen molecule can take two orientations, parallel and perpendicular, with respect to the field of the Na⁺ cation. In NaCaA the adsorption site is in front of a Na⁺ or Ca²⁺ cation in a site S_I. It was shown that the frequency shift depends strongly on the location of the cation in the 6-ring. In CaA, the strongest site seems to be located near a Ca²⁺ cation in a S_{II} site in a 8-ring window. The frequency shifts, calculated for all these adsorption sites, depend strongly on the variation of the quadrupole moment and of the parallel and perpendicular polarizability component of the admolecule with respect to the normal coordinate, which are only known up to first order. By adjusting the computed shift to the experimental one, we have been able to calculate a crude value of the second derivative of these molecular quantities with respect to the normal coordinate.

1. Introduction

In the previous paper we presented the analysis of the shape and intensity of the infrared spectra of the oxygen molecule adsorbed in A-type zeolites.¹ The frequency shift with respect to the gas phase frequency is related to the variation of the interaction potential with the normal coordinate Q of the sorbed molecule. Its numerical determination requires an exhaustive description of the zeolite–molecule interaction, but may be performed, in a first approximation, without dynamical calculations. Buckingham derived an analytical expression for the frequency shift that depends on the first and second derivatives of the interaction potential with respect to Q and therefore of the variation with Q of the molecular quantities, such as polarizabilities and multipole moments.² These variations are known for very few molecules (H₂ and N₂ for example^{3,4}). This calculation has been applied in our laboratory for a number of years to describe the frequency shift of diatomic homonuclear molecules (H₂, N₂, O₂) in NaA zeolite.⁵ The latter system showed up as particularly interesting: two infrared bands in the spectrum of O₂ were associated with two orientations of the sorbed molecule with respect to the electric field. However, this interpretation lies on a very simple model of zeolite NaA, namely, as a single Na⁺ cation. Moreover, there is a lack of data concerning the molecular quantities of the oxygen molecule. Buckingham's formula still is now a well-established tool for interpreting the frequency shift $\Delta\sigma$ of simple molecules in zeolites.⁶ Recently, the calculation of the vibrational frequency shift of H₂ has been used as a method for estimating the ionic charges in NaA.⁷ In this paper we present a similar analysis of the frequency shift of O₂ sorbed in sodium and calcium A zeolites. Extensive experimental data have been recorded in

our laboratory,^{1,8} showing noticeable differences in the spectra of O₂ in these zeolites. The aim of this study is 3-fold: first, to verify the results obtained on the O₂–NaA systems with the simple model mentioned above; second, to study how the lack of data on the molecular constants influences the determination of the frequency shift; third, to pinpoint by the analysis of the oxygen frequency shift the differences between three zeolites having the same structure but different cations.

Details about the systems have been given in the preceding article,¹ together with the experimental part of the study. Table 1 reports the observed frequency shifts of O₂ in NaA, NaCaA, and CaA, as well as the isosteric heats of adsorption, calculated from the analysis of the intensity of the spectra.

2. Theoretical Section

A. Interaction Potential. The zeolite is represented by point charges placed at the crystallographic positions of the ions. The electrostatic part of the interaction potential consists of an expansion along the permanent and induced multipole moments of the molecule. As usual, the expansion was limited to the first significant terms: quadrupole and induced dipole moment.

$$U_{\text{elec}} = \frac{1}{2} \sum_i q_i \Theta_{zz} R_i^{-3} (3 \cos^2 \phi_i - 1) - \frac{1}{2} \left[\alpha_{\perp} \left[\left(\sum_i \frac{q_i x_i}{R_i^3} \right)^2 + \left(\sum_i \frac{q_i y_i}{R_i^3} \right)^2 \right] + \alpha_{\parallel} \left(\sum_i \frac{q_i z_i}{R_i^3} \right)^2 \right] \quad (1)$$

The sum refers to all ions i of the zeolite that are taken into account; q_i is the charge of the i th ion, R_i is its distance to the center of mass of the molecule, x_i , y_i , and z_i are the components of R_i in the molecular reference frame, ϕ_i is the angle between the electric field of the ion and the molecular axis, Θ_{zz} is the molecular quadrupole, and α_{\parallel} and α_{\perp} are the parallel and perpendicular components of the polarizability tensor.

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TABLE 1: Frequency Shift and Isotheric Heat of Adsorption of O₂ Sorbed in A-Type Zeolites

	NaA		NaCaA	CaA
	HF	LF		
$\Delta\sigma$ (cm ⁻¹)	+9	-2	-2	shoulder: -6
Q^{st} (kJ/mol)	15.4	11.4	15.3	18.6

TABLE 2: Molecular and Spectroscopic Constants of O₂

quadrupole moment ^{20,5}	$\Theta_{zz} = 1.30 \times 10^{-40} \text{ C m}^2$, $\partial\Theta_{zz}/\partial\rho = 3.34 \times 10^{-30} \text{ C m}$
polarizability ^{21,19}	$\alpha_{\parallel} = 2.61 \times 10^{-40} \text{ C m}^2 \text{ J}^{-1}$, $\partial\alpha_{\parallel}/\partial\rho = 3.80 \times 10^{-30} \text{ C m J}^{-1}$, $\alpha_{\perp} = 1.35 \times 10^{-40} \text{ C m}^2 \text{ J}^{-1}$, $\partial\alpha_{\perp}/\partial\rho = 0.53 \times 10^{-30} \text{ C m J}^{-1}$
dimensions ^{22,10}	$\rho_e = 1.207 \text{ \AA}$, $R_{\parallel} = 2.08 \text{ \AA}$, $R_{\perp} = 1.48 \text{ \AA}$
spectroscopic constants ²²	$\omega_e = 1580.36 \text{ cm}^{-1}$, $B_e = 1.446 \text{ cm}^{-1}$, $a = -2.99$ dimensionless

The second part of the interaction potential is represented by an ion–molecule Lennard-Jones potential:

$$U_{\text{LJ}} = -\sum_i R_i^{-6} [3(C_{\parallel}^i - C_{\perp}^i) \cos^2 \phi_i + C_{\parallel}^i + 5C_{\perp}^i] + \sum_i R_i^{-12} [B_{\parallel}^i \cos^2 \phi_i + B_{\perp}^i \sin^2 \phi_i] \quad (2)$$

The parallel and perpendicular dispersion constants are calculated using the Slater–Kirkwood formula:⁹

$$C_{\text{or}}^i = \frac{1}{4} e^2 a_0^{1/2} \frac{\alpha_i \alpha_{\text{or}}}{(\alpha_i/N_i)^{1/2} + (\alpha_{\text{or}}/N)^{1/2}} \quad (3)$$

e is the electronic charge, a_0 is Bohr's radius, α_i is the ionic polarizability, and N_i the number of electrons of the ion, while α_{or} stands for the parallel or perpendicular molecular polarizability and N represents the number of electrons of the molecule.

The repulsive constant B_{\parallel}^i (respectively B_{\perp}^i) is determined by minimizing the molecule– i th ion interaction in the case of a parallel (respectively perpendicular) orientation of the molecular axis with respect to the ion, at a distance $R_{i0} = R_{\parallel} + \sigma_i$ (respectively R_{\perp}). σ_i is the radius of the i th ion, and R_{\parallel} and R_{\perp} are the dimensions of the O₂ molecule parallel and perpendicular to the molecular axis. These dimensions, for the free molecule, are given by the surface of isoelectronic density $Q = 0.002$ au, which contains 95% of the electron probability.¹⁰ The molecular constants needed in the calculation are listed in Table 2.

B. Zeolite Model. Dimension. The question of the dimension of the crystal to study is rather complex, as many different computation techniques can be applied. The Ewald summation technique, for example, treats long-range forces well, but cannot be fully applied here because of the disorder of the Na⁺ and Ca²⁺ cations. However, it has been shown by Boumiz *et al.* that good quantitative results can be obtained by taking into account the ions of only seven cavities¹¹ and typical cutoffs of around 10 Å.¹² Therefore, we chose to build two simple spherical microdomains, with a radius of 14 and 27 Å, centered at the center of the zeolite α cavity. These microcrystals are neutral and contain, respectively, 516 and 3696 ions. These microcrystals are not large enough for the Coulombic energy to converge; however, as the adsorbed molecule bears no partial charge, the electrostatic part of the interaction energy decreases as R^{-3} , that is, much faster than the Coulombic energy. Preliminary results¹³ have shown that the difference between the interaction energies calculated for the two microcrystals does not exceed 1.5%, while the difference in the frequency shift is

TABLE 3: Dependence of Ionic Radius and Polarizability on q_0 (in au)

	Na	O	Si	Al
radius	a -1.058	-0.548	-0.554	-0.383
$\sigma(X) = aq(X) + b$	b 2.91	2.872	2.23	2.098
polarizability	a 27.98	9.38		
$\alpha(X) = aq(X) + b$	b -29.78	-7.55		
polarizability	a		0.013	0.109
$\alpha(X) = a \exp[(q(X) - b)/c]$	b		12.39	10.70
	c		-19.13	19.40

0.5 cm⁻¹ at the most. These good results are mainly due to the similarity between the two microcrystals, as they both obey the conditions $\sum_i q_i = 0$ and $\sum_i q_i \alpha_i = 0$ ($\alpha = x, y, \text{ or } z$). This justifies our model; all results presented in section 3 are computed for the smaller of the microcrystals.

Charge Distribution. As the cationic sites are only partially occupied, which is not realistic on the microscopic level, one has to choose a distribution of the cations over these sites. We chose the distribution of the cations as follows: the position of the ions inside the central cavity (which is the only cavity for which the interaction is computed) is taken so that Coulombic energy is minimum; then, the position of the ions in the neighboring cavities is chosen so that the center of the positive charges (cations) coincides with the center of the negative charges (anionic framework). Note that this condition cannot be achieved in NaA, due to the small size of the microcrystal considered; a slight displacement remains, about 0.1 Å. A number of distributions are energetically equivalent. To investigate their influence, five different distributions were studied in NaA. For Na₂Ca₅A two distributions were taken into account, while in Na₄Ca₄A there is no ordering problem: the optimal distribution is completely symmetrical and is found by alternating Na⁺ and Ca²⁺ cations in the neighboring S₁ sites. As we have seen, in CaA one of the Ca²⁺ cations lies in the 8-ring window's plane, thus belonging to two cavities at the same time. There is a strong probability of finding cavities with two or more windows occupied by Ca cations. Therefore, we studied two cationic distributions: with one or two windows occupied by Ca²⁺ cations.

Charges used to model the zeolite differ between authors; oxygen in NaA, for example, can have a charge from $-0.25e$ ¹⁴ to $-1.5e$.¹⁵ The model proposed by Larin *et al.*⁷ takes into account these variations, through a parameter q_0 referred to as *ionicity*. The charges are determined by the relation

$$\frac{n_{\text{Ca}}}{12} q_{\text{Ca}} + \frac{n_{\text{Na}}}{12} q_{\text{Na}} + q_{\text{Si}} + q_{\text{Al}} = |4q_0| = q_0$$

n_{Ca} and n_{Na} denote respectively the number of Ca²⁺ and Na⁺ ions per unit cell. The ratio $q_{\text{Si}}/q_{\text{Al}}$ is found for similar compounds in the literature: $q_{\text{Si}}/q_{\text{Al}} = 0.975$.¹⁶ Supposing that the cationic charges are integral, $q_{\text{Na}} = +1e$ and $q_{\text{Ca}} = +2e$, then the charge of each of the ions of the zeolite is uniquely determined by q_0 .

Similarly, the ionic quantities (radius and polarizability) are functions of the ion charge and thus of q_0 . The dependence of these values on the ionic charge is given in Table 3, while Figure 1 depicts their variation with the ionicity parameter q_0 .

The previous estimation of q_0 led to the value $q_0 = 5.7$;⁷ it corresponds to relatively high values of the framework charges: $q_0 = -1.5e$, $q_{\text{Si}} \approx q_{\text{Al}} = +2.5e$. These partial charges are quite close to charges recently calculated *ab initio* in aluminosilicates.¹⁵ In a first step of the calculation we shall use the same value of q_0 .

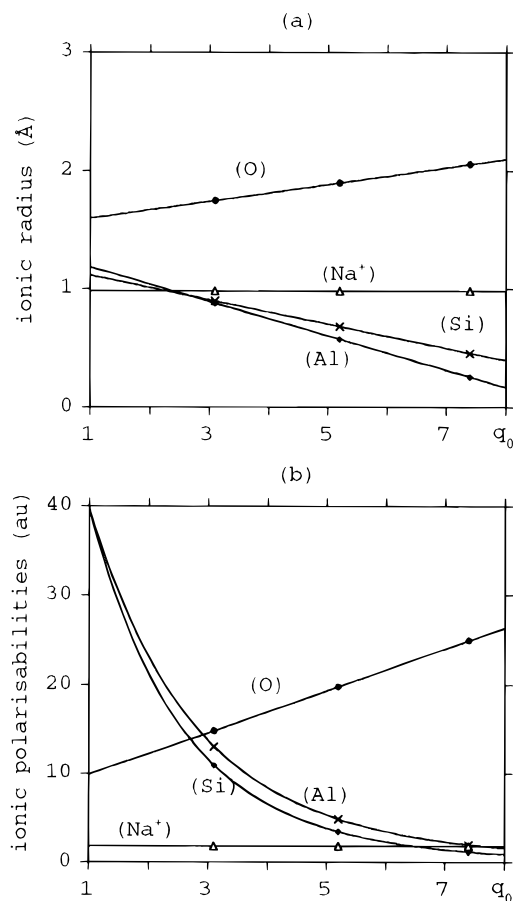


Figure 1. (a) Radius and (b) polarizability of the elements as a function of the ionicity parameter q_0 : (●) O; (Δ) Si; (×) Al; and (◆) Na.

C. Frequency Shift Calculation. The frequency shift $\Delta\sigma$ of the sorbed molecule can be written as⁷

$$\Delta\sigma = \frac{1}{hc} [(E_1^{(a)} - E_0^{(a)}) - (E_1^{(f)} - E_0^{(f)})] \quad (4)$$

$E_0^{(a)}$ and $E_1^{(a)}$ are the energies of the ground state and first excited state of the sorbed molecule; $E_0^{(f)}$ and $E_1^{(f)}$, the corresponding energies for the free molecule. The determination of these energies by a perturbation treatment leads to Buckingham's formula:

$$\Delta\sigma = \frac{B_e}{hc\omega_e} [U'' - 3aU'] \quad (5)$$

B_e and ω_e are the rotational constant and harmonic frequency of the molecule, respectively, and a is the anharmonicity of the electronic potential V_{el}^r . $U' = (\partial U / \partial Q)$ and $U'' = (\partial^2 U / \partial Q^2)$ are the first and second derivatives of the interaction energy U with respect to the normal coordinate of the oxygen molecule $Q = \mu^{1/2}\rho$.

The energy levels E_0 and E_1 can also be calculated numerically by solving the radial Schrödinger equation for the motion of the nuclei, with a proper integration program. We used LEVELS created by R. J. Leroy,¹⁷ which is based on Numerov–Cooley's algorithm.

One needs the variation of the interaction potential with the internuclear coordinate ρ to calculate the frequency shift. The dependence of the interaction potential is implicit in eqs 1 and 2, as it comes entirely from the dependence of the molecular quantities (components of the polarizability tensor $\alpha_{||}$ and α_{\perp} and of the quadrupole moment Θ_{zz} and dimensions $R_{||}$ and R_{\perp}

of the molecule). Unfortunately, the variation of these quantities for the oxygen molecule is only poorly known.⁵ Therefore, it was approached by a Taylor series around the equilibrium internuclear coordinate ρ_e :

$$X(\rho) = X(\rho_e) + \left(\frac{\partial X}{\partial \rho} \right)_{\rho_e} (\rho - \rho_e) + \frac{1}{2} \left(\frac{\partial^2 X}{\partial \rho^2} \right)_{\rho_e} (\rho - \rho_e)^2 + \dots$$

(X represents $\alpha_{||}$, α_{\perp} , Θ_{zz}) (6)

The second derivatives of α and Θ_{zz} with respect to ρ have not been determined; in a first approach we set these quantities to 0. In section 3.D the consequences of this approximation will be analyzed. The variation of the molecular dimensions is chosen so as to leave the molecular volume (calculated as an ellipse) constant:

$$R_{||}(\rho) = R_{||}(\rho_e) + (\rho - \rho_e) \quad (7)$$

$$R_{||}(\rho) R_{\perp}^2(\rho) = R_{||}(\rho_e) R_{\perp}^2(\rho_e) \quad (8)$$

3. Results and Discussion

A. NaA. The first step of the calculation consists in determining the adsorption sites for which the frequency shift shall be calculated. Five different distributions of the Na⁺ ions in the microcrystal were studied. Due to the inhomogeneity of the cationic repartition, these five configurations induce a distribution of the minima of the interaction energy (IE) in the cavity. Consequently, there is also a distribution of the frequency shifts. However, in all five configurations the energy minima are located in the same regions of the cavity; we group those minima, which have close characteristics but not exactly the same energy, in the same class. Four classes of minima are found in NaA. Figure 2a,b indicates the adsorption equipotentials of O₂ in the cavity of NaA, thus showing the relative depth of the energy minima of each class.

The deepest energy minima are close to the Na ion in a S_{III} site; their IE ranges between −26 and −24 kJ/mol. The molecules in these minima are oriented parallel to the electric field with values varying between 1.4×10^{10} and 1.5×10^{10} V/m. $\Delta\sigma$ ranges between −1 and +5 cm^{−1}. The position of the molecule corresponding to this minimum is depicted in Figure 3a.

Minima of the second class are also located close to the Na_{III} ion. However, the IE is less negative (from −22 to −24 kJ/mol), and the molecule takes a perpendicular orientation with respect to the electric field. The latter is stronger than in the first class: from 1.8×10^{10} to 2.0×10^{10} V/m. The corresponding frequency shift is negative: between −9 and −12 cm^{−1}. The position of the O₂ molecule is depicted in Figure 3b. In both the first and second classes the electric field mainly originates from the Na⁺ cation in the S_{III} site.

Third and fourth class contain minima which have lower absolute values: from −17 to −10 kJ/mol. They are located respectively close to the Na⁺ ion in a S_{II} site of an 8-ring window and in a S_I site. The molecules have no specific orientation with respect to the electric field, and the corresponding frequency shift ranges between −5 and +5 cm^{−1}.

The five distributions of the positions of the Na_{III} cations do not generate enough configuration of the IE minima to perform any statistics, and thus no average quantity with a physical meaning is available. Therefore, in the following discussion, the values corresponding to the deepest potential well for each of the minima classes shall be used. Table 4 gives the quadrupolar, inductive, dispersive, and repulsive contributions to the IE, in the four classes of minima. One can see that in all

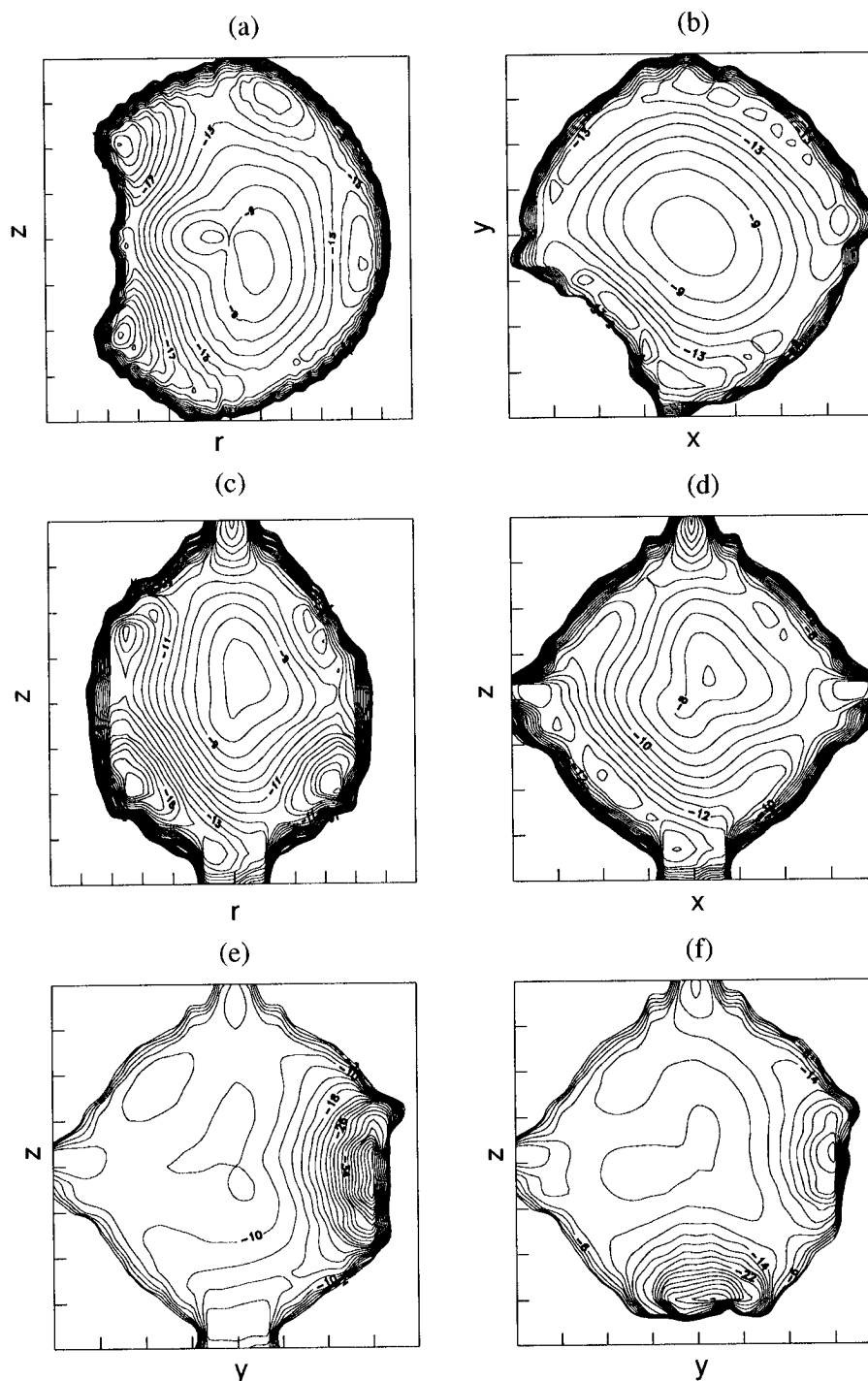


Figure 2. Adsorption equipotentials of O_2 in NaA, NaCaA, and CaA, showing the preferred adsorption sites. The scale is in angstroms. (a and b) NaA, planes (110) and (001). The Na_{III} cation is placed at coordinates $X = -3.536 \text{ \AA}$, $Y = -3.536 \text{ \AA}$, $Z = 0$. The O_2 molecule lies in the plane, perpendicular to the axis passing by the center of the cavity and the center of mass (COM) of the molecule in (a), and parallel to this axis in (b). The separation between the levels is 1 kJ/mol. (c and d) Na_2Ca_5A , planes (110) and (001). The molecule has the same orientation in (c) as in (a) and in (d) as in (b). The separation between the levels is 0.5 kJ/mol. (e and f) CaA1 and CaA2 (see text), plane (100). The molecule lies in the (100) plane, perpendicular to the axis passing through the center of the cavity and the COM of the molecule. The separation between the levels is 2 kJ/mol.

cases the quadrupolar energy remains very low, which reflects the low value of the quadrupolar moment of the oxygen molecule more than the gradient of the electric field. The dispersive energy is almost the same in all four minima; the main difference in the IE comes from the inductive energy and thus from the electric-field strength. Table 5 shows the contributions to the frequency shift, as calculated using Buckingham's formula ($\Delta\sigma_B$) and by numerical solution ($\Delta\sigma_N$). The two methods give very similar results although not identical. The contributions to the shift are obtained by replacing in the

frequency shift calculation the total interaction potential $U(\rho)$ by each contribution. Note that following this procedure, $\Delta\sigma_N$ is not equal to the sum of the respective contributions, while $\Delta\sigma_B$ is. The difference represents the higher order terms, which are not taken into account in Buckingham's formula. This proves the validity of the latter and also shows its limits. All $\Delta\sigma$ values have been calculated by numerical solution. One can see that the dispersive contribution to the shift is very similar in the four minima. On the other hand, the quadrupolar contribution is no longer negligible and reflects the orientation

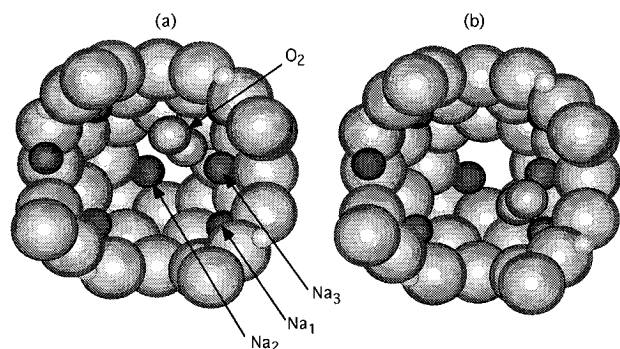


Figure 3. View of the O_2 molecule in the two main adsorption sites of NaA. Only the oxygens and sodiums are displayed. The electric field in these two adsorption sites mainly originates from the Na^+ cation in the S_{III} site.

TABLE 4: Contributions to the O_2 /NaA Interaction Energy in the Deepest Potential Well of Each Class of Energy Minima (All Values in kJ/mol)

class	U_{total}	U_{quad}	U_{ind}	U_{disp}	U_{rep}
1	-26.6	-2.6	-16.1	-23.3	+15.4
2	-21.9	+1.1	-12.3	-23.9	+13.2
3	-19.8	-2.8	-7.1	-23.0	+13.1
4	-17.9	-0.5	-5.6	-21.1	+9.3

of the molecule in the electric field. Note that the inductive contribution is always negative and is compensated by the repulsive contribution, so that the sign of the total shift appears to be mainly related to the quadrupolar contribution and thus to the orientation of the molecule.

The correspondence between the infrared bands and the minima classes is based upon the strength of the interaction energy and of the electric field in the classes. From these criteria the high-frequency band on the O_2 /NaA spectrum is assigned to the molecules adsorbed in the first class of minima and the low frequency band to the molecules in the second class. By comparison with Table 1, one sees that the difference between the energy of these two minima (4.7 kJ/mol) is close to the difference in the heats of adsorption deduced from the IR band intensities (4 kJ/mol). On the other hand, the calculated frequency shifts are rather different from the experimental shifts, although the difference between the high- and low-frequency shift is close to the experimental value. These shifts have been computed with $q_0 = 5.7$ adjusted to reproduce the shift of H_2 in NaA. However, we have shown in a preceding paper¹⁸ that no value of the ionicity q_0 leads to a match between experimental and calculated shifts. Therefore, in the next part of the calculation the same value, $q_0 = 5.7$, will be used.

B. NaCaA. Two classes of minima were found in NaCaA, for both Na_4Ca_4A and Na_2Ca_5A (cf. Figure 2c,d). The deepest potential wells are located near the 6-rings between the α - and β -cages and have to be associated with the main band of the IR spectrum. The IE for the most attractive wells amounts to -22.3 kJ/mol in Na_2Ca_5A and -18.3 kJ/mol in Na_4Ca_4A . The electric field is 1.3×10^{10} V/m in Na_2Ca_5A and 1.1×10^{10} V/m in Na_4Ca_4A ; no precise orientation is found. The frequency

shift is -8 cm^{-1} in Na_2Ca_5A and $+3.2 \text{ cm}^{-1}$ in Na_4Ca_4A . Significant differences appear between the two structures: in Na_2Ca_5A a minimum exists near each 6-ring, whether it is empty or occupied by an Na^+ or Ca^{2+} cation; in Na_4Ca_4A only the 6-rings with Ca^{2+} cation form a minimum. This difference is due to the location of the cations in the 6-rings: in Na_2Ca_5A the Na^+ is located inside the α -cage and the Ca^{2+} in the β -cage, thus being much more screened by the framework oxygens; in Na_4Ca_4A it is just the opposite, and thus the interaction with the Ca^{2+} cation becomes predominant. Note that although in Na_4Ca_4A the molecules interact with cations that bear a larger effective charge (as they are less screened by the framework) than in Na_2Ca_5A , the calculated electric field is lower; this shows that in NaCaA the electric field mainly originates from the framework oxygens.

Minima of the second class are located near the 8-ring windows of the cavity. However, their energy is much lower in absolute value (≈ 12 kJ/mol), which reflects the low electric field: $(0.4-0.8) \times 10^{10}$ V/m; the frequency shift is negative in Na_2Ca_5A (-10 cm^{-1}) and positive in Na_4Ca_4A ($+1.4 \text{ cm}^{-1}$). Molecules at these sites may be responsible for the second weak band that appears at high pressure in the O_2 /NaCaA spectrum.

As in NaA, the right order of magnitude is found for both the interaction energy and the frequency shift; however, the discrepancy between the experimental and calculated shift does not allow any attribution of the observed frequency shift to the particular Na_2Ca_5A or Na_4Ca_4A structure.

C. CaA. We first recall that two different distributions of the Ca^{2+} cations were studied in CaA: in the first (hereafter CaA1) a single 8-ring window is occupied by a Ca^{2+} cation, whereas two windows are occupied in the second (CaA2). Three classes of minima are found. The deepest minima occur near the Ca^{2+} cation of the window, the molecular axis being parallel to the electric field (cf. parts e and f of Figure 2). Their IE amount to -74.1 kJ/mol in CaA1 and -60.9 kJ/mol in CaA2, arising for the most part from the inductive interaction with the strong electric field (3.3×10^{10} V/m in CaA1 and 3.0×10^{10} V/m in CaA2). One sees that the second Ca^{2+} cation in the window of CaA2 attenuates the electric field in front of the first and thus the absolute value of the IE. The corresponding frequency shifts are -20.4 cm^{-1} in CaA1 and -26.1 cm^{-1} in CaA2. A second class of minima occurs near the Ca^{2+} cation of the window, but the molecules are perpendicularly oriented with respect to the electric field; a third class corresponds to the molecules near the Ca^{2+} cations in the S_I sites. These minima have much lower energy -45 and -30 kJ/mol, respectively; as the IR spectrum of O_2 sorbed in CaA only shows a single induced band, we shall discuss only the first class of the potential wells.

There is a dramatic discrepancy between the calculated IE in this site and the heat of adsorption as determined from the infrared intensities, when compared to the relatively small differences that have been found with NaA and NaCaA. The influence of the ionic charges and of the hyperpolarizability and hexadecapole moment of O_2 have been considered,¹³ but these minor corrections are not sufficient to describe correctly

TABLE 5: Contributions to the O_2 /NaA Frequency Shift (All Values in cm^{-1})

class	$\Delta\sigma_{total}$		$\Delta\sigma_{quad}$		$\Delta\sigma_{ind}$		$\Delta\sigma_{disp}$		$\Delta\sigma_{rep}$	
	N^a	B^b	N	B	N	B	N	B	N	B
1	-1.4	-2.1	+5.5	+5.5	-19.3	-19.2	-12.5	-12.6	+24.2	+24.2
2	-9.1	-9.4	-2.3	-2.3	-6.0	-6.1	-11.9	-11.9	+10.9	+10.8
3	+3.5	+3.1	+6.0	+6.0	-6.9	-7.0	-12.2	-12.2	+16.4	+16.3
4	-6.2	-6.2	+1.1	+1.1	-6.1	-6.2	-11.2	-11.2	+10.0	+9.9

^a Numerical calculation. ^b Calculation applying Buckingham's formula.

TABLE 6: Parameters Describing the Frequency Shift (cm^{-1}) as a Function of the Second Derivatives (au) of α and Θ_{zz} with Respect to ρ^a

potential well	$\Delta\sigma_0$	a	b	c
NaA class 1	-1.4	+3.3	-0.38	-0.31
NaA class 2	-9.1	-1.4	-0.13	-0.75
Na ₂ Ca ₅ A class 1	-7.9	+1.2	-0.35	-0.26
Na ₄ Ca ₄ A class 1	+3.2	+2.3	-0.17	-0.34

^a Parameters a , b , and c are in cm^{-1}/au .

TABLE 7: Values of the Second Derivatives of the Oxygen Quadrupole Moment and Polarizabilities with Respect to the Internuclear Coordinate^a

	Θ''_{zz}	$\alpha''_{ }$	α''_{\perp}
adjustment with Na ₂ Ca ₅ A	$+1.3 \pm 3.1$	-7 ± 30	-11 ± 15
adjustment with Na ₄ Ca ₄ A	-7.0 ± 3.1	-105 ± 42	$+21 \pm 14$
N ₂ ^{3,23}	0.51	7.46	2.26

^a Results of the adjustments on NaA, Na₂Ca₅A, and Na₄Ca₄A. All values are given in atomic units.

the IE in CaA. As we are not interested in depicting the absolute values of the interaction energies, no further attempt to correct the results in CaA has been made.

D. Frequency Shift. Both in NaA and NaCaA, the calculated frequency shifts are noticeably different from the experimental ones, although rather close. We shall now prove that this discrepancy can be attributed to the truncation of the expansion of the molecular quantities as a function of the internuclear coordinate.

In each potential well that has been found in the preceding sections, the frequency shift can be written as a function of the derivatives of the molecular quantities with respect to the internuclear coordinates: $\Delta\sigma = f(\Theta''_{zz}, \alpha''_{||}, \alpha''_{\perp})$, where X'' denotes the second derivative with respect to ρ of the quantity X . Calculating $\Delta\sigma$ for different values of X'' , its dependence is found to be almost linear over a range that goes up to ± 20 au around $X'' = 0$. Thus, it can be written as

$$\Delta\sigma = \Delta\sigma_0 + a\Theta''_{zz} + b\alpha''_{||} + c\alpha''_{\perp} \quad (9)$$

Here a , b , and c are parameters, listed in Table 6, for the calculated frequency shifts that correspond to the experimental infrared bands. Three experimental shifts can be compared with the calculated ones: two in NaA and one in NaCaA; as the IE in CaA are overestimated, we shall not consider the corresponding shift. As eq 9 contains three unknown parameters, adjusting these parameters so that the calculated shifts match the experimental ones is straightforward. Two adjustments were performed: (i) comparison between the experimental shifts in NaA and NaCaA with the calculated shifts in NaA and Na₂Ca₅A; (ii) comparison between the experimental shifts in NaA and NaCaA with the shifts calculated in NaA and Na₄Ca₄A. The values of the second derivatives of the quadrupole moment and polarizabilities of the oxygen molecule resulting from these adjustments are displayed in Table 7. The third line gives the same data for the nitrogen molecules, known from *ab initio* work.^{3,19} The uncertainties are computed from the uncertainties of the experimental frequencies, namely, the half-width of the infrared bands ($\approx 3 \text{ cm}^{-1}$).

The adjustment using $\Delta\sigma$ calculated in Na₄Ca₄A leads to X'' values that are at least 1 order of magnitude higher than those of nitrogen and can be regarded as unrealistic. On the other hand, the adjustment on Na₂Ca₅A leads to X'' values that are quite close to those of nitrogen. From this comparison, two conclusions may be drawn: (i) the adjustment is possible with physically acceptable values of the molecular quantities, and

(ii) the NaCaA zeolite used for the experimental study appears to have a cationic distribution closer to Na₂Ca₅A than to Na₄Ca₄A.

Replacing the adjusted X'' values in the calculation of the frequency shift for the second adsorption site in Na₂Ca₅A leads to a shift of $\Delta\sigma = -2.5 \text{ cm}^{-1}$, which is close to the frequency of the shoulder band on the infrared spectrum of O₂ in NaCaA. Furthermore, the same X'' reduces the frequency shift in CaA from -20.4 to $+1 \text{ cm}^{-1}$, once again very close to the experimental shift (0 cm^{-1}). These agreements clearly add to the validity of the procedure. The rather crude values of the second derivatives of Θ_{zz} , $\alpha_{||}$, and α_{\perp} derived from this analysis prove that the method is applicable; a quantitative analysis of the frequency shift, however, clearly requires *exact* knowledge of the dependence on the internuclear coordinate of *all* molecular quantities. On the other hand, the magnitude of the interaction energy is of little importance in the derivation of the shift (which is mathematically evident in eq 5).

4. Conclusion

This study shows that the position of the exchangeable cation in the zeolite framework strongly influences the interaction with O₂. For a small molecule, like O₂, the van der Waals contribution to the interaction energy (especially the dispersive part) is very similar for all minima. The main difference then originates in the electrostatic interaction, that is, in the electric field. In NaA, the Na_{III} cation lies inside the α -cage and is barely screened by the oxygen anions. As a consequence, the electric field mainly originates from this ion. This explains the good accordance between our results for NaA and the calculation of ref 5, where the zeolite was modeled by a single Na⁺ cation. On the other hand, the cations in NaCaA all occupy S_I sites in the 6-rings and are more screened by the oxygens. The interaction cannot be represented, even qualitatively, by a single ion. In CaA, the strong interaction calculated originates from the electrostatic interaction with the field due to the barely screened Ca cation in the window. However, the discrepancy between the magnitude of the interaction calculated and that determined from experimental data raises questions about the applicability of the model to CaA.

From the discussion on the frequency shift, it follows that precise knowledge of the variation of the molecular quantities with the normal coordinate is required to compute a reliable value of the shift. Nevertheless, orders of magnitude and relative shifts in NaA have been calculated quite accurately only with dependence of the first order. By comparison to the experimental shifts, we have calculated a crude value of the second-order dependence of the polarizability and the quadrupole moment of oxygen as a function of the normal coordinate. However, these values have large uncertainties, and to get any quantitative results on the frequency shift, more precise values need to be calculated, for example from *ab initio* calculations.

References and Notes

- (1) Jousse, F.; Cohen de Lara, E. Submitted to *J. Phys. Chem.*
- (2) Buckingham, A. D. *Trans. Faraday Soc.* **1960**, *56*, 753.
- (3) Amos, R. D. *Mol. Phys.* **1980**, *39*, 14.
- (4) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1967**, *46/4*, 14226.
- (5) Cohen de Lara, E. *Mol. Phys.* **1989**, *66*, 479.
- (6) Yamazaki, T.; Watanuki, I.; Ozawa, S.; Ogino, Y. *Mol. Phys.* **1991**, *73*, 649.
- (7) Larin, A. V.; Cohen de Lara, E. *J. Chem. Phys.* **1994**, *101*, 8130.
- (8) Soussen-Jacob, J.; Tsakiris, J.; Cohen de Lara, E. *J. Chem. Phys.* **1989**, *91*, 2649.
- (9) Salem, L. *Mol. Phys.* **1960**, *3*, 441.

- (10) Bader, R. F. W.; Henneker, W. H.; Cade, P. E. *J. Chem. Phys.* **1967**, *46*, 3341.
- (11) Boumiz, A.; Cartigny, J.; Cohen de Lara, E. *J. Chem. Phys.* **1992**, *96*, 5419.
- (12) Smirnov, K. S.; LeMaire, M.; Brémard, C.; Bougeard, D. *Chem. Phys.* **1994**, *179*, 445.
- (13) Jousse, F. Ph.D. Thesis, Université de Paris, 1994.
- (14) Bezus, A. G.; Kiselev, A. V.; Lopatkin, A. A.; Du, P. Q. *J. Chem. Soc., Faraday Trans.* **1978**, *2*, 367.
- (15) Hess, A. C. *J. Phys. Chem.* **1994**, *98*, 4463.
- (16) Barinskii, R. L.; Nefedov, V. I. *X-Ray Spectral Determination of Atomic Charges in Molecules*; Nauka: Moscow, 1966.
- (17) Leroy, R. J. Dept. of Chemistry, University of Waterloo, Waterloo, Ontario N2L3G1, Canada, 1989.
- (18) Larin, A. V.; Jousse, F.; Cohen de Lara, E. In *Proceedings of the 10th International Zeolite Conference*; Weitkamp, J., Karge, H. G., Pfeifer, H., Hölderich, W., Eds.; Elsevier: Amsterdam, 1994; p 2147.
- (19) Murphy, W. F.; Holzer, W.; Bernstein, H. J. *Appl. Spectrosc.* **1969**, *23*, 211.
- (20) Strogryn, D. E.; Strogryn, A. P. *Mol. Phys.* **1966**, *11*, 370.
- (21) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; J. Wiley & Sons: New York, 1954.
- (22) Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand: Princeton, NJ, 1939.
- (23) Nesbet, R. V. *J. Chem. Phys.* **1964**, *40*, 3619.

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