Rotation of molecules and ions in confined spaces: a first-principles simulation study

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Abstract
A simulation study on the rotational behavior of neutral and charged molecular systems hosted in zeolitic cages is presented here. Synthetic sodalites containing both molecular \((\text{O}_2)\) and anionic \((\text{NO}_2^-)\) species and an hydrated Ti-offretite have been simulated by first-principles molecular dynamics. Our results show that both host–guest and guest–guest interactions directly influence the rotational motion of the caged species.

Keywords: Rotation; First-principles simulations; Zeolites; Confined systems

1. Introduction
Zeolites are crystalline, porous, aluminosilicate materials able to selectively incorporate and exchange ions, molecules or clusters within the void space and interconnecting channels. Their characteristic properties, i.e. thermal and chemical stability, shape-selectivity and the presence of a regular distribution of cavities of well-defined size, make zeolites materials of primary importance in both traditional industrial applications, such as detergent and oil industry [1], and advanced applied research on the design and synthesis of new nanostructured materials [2]. In addition, zeolites are the subject of intense study in crystallography and earth sciences, focused on the characterization of their structure as well as on their behavior under temperature and pressure conditions different from the ambient ones [3].

It is clear that an atomic-level knowledge of the systems hosted into the zeolitic cages and their interactions with the framework is of topic relevance for a deeper understanding of the experimentally observed macroscopic phenomena. This could lead in turn to major improvements in technologically relevant processes involving zeolitic materials. First-principles molecular dynamics simulations [4] may provide a hint in this direction, owing to their ability to model the finite-temperature behavior of condensed phase systems with the accuracy of static quantum chemical calculations. The work presented here is a theoretical study on the dynamics of neutral and charged guest systems confined in zeolitic cages. Particular attention has been devoted to the analysis of...
the rotational and librational motion of the confined systems, with the purpose to acquire insight about the factors affecting them. Owing to the availability of void space in zeolitic materials, the rotational behavior of the guest system should resemble the gas-phase one rather than the one typical of molecules in a condensed-phase environment. On the other hand, spatial confinement, electrostatic long range interactions with the framework and guest–guest interactions should make the picture rather different from that shown by a free rotating molecule. For instance, host–guest interactions lead in general to a coupling of the guest to the framework motion, while guest–guest interactions may hinder rotational motion along selected directions. Quantitative information on these factors can be drawn by studying the rotational motion of systems differing in size, charge and symmetry in zeolites having different cage size and chemical composition.

The experimental frequencies of the rotational and librational modes of the guest system could be in principle obtained by far-IR and Raman spectra. However, these modes absorb in general at frequencies lower than 1000 cm\(^{-1}\), i.e. in regions where intense and broad framework bands are also present and often completely hide the libration bands of the guest. Simulations are an extremely useful tool in this respect, as the contribution to the total spectrum of distinct modes or groups of atoms can be calculated from the MD trajectory, thus providing information which would not be directly accessible to experiments.

A previous simulation study on nitrite sodalite (Na\(_8\)[Al\(_6\)Si\(_6\)O\(_{24}\])(NO\(_2\))\(_2\)) [5] has shown that the experimentally observed orientational disorder of the nitrite anion [6] is actually due to its rotational motion inside the cage, which is dynamically coupled to low-frequency framework vibrational modes [7]. Here we compare the rotational behavior of NO\(_2^–\) with that of the larger NO\(_3^–\) anion in the same sodalite cage in order to investigate the effects of the guest’s size. Moreover, information on the role played by the guest–guest interactions has been obtained from the simulation of a sodalite cage including both a NO\(_2^–\) anion and another guest molecule, namely molecular oxygen.

Finally, we examined how the size and the morphology of the cage may affect the guest’s rotational motion by studying the dynamics of water molecules hosted in two different cages of the zeolite offretite.

2. Systems and simulation details

Sodalites are zeolites formed by corner-sharing TO\(_4\) tetrahedra (T = Si, Al) characterized by cubo-octahedral cages (also known as \(\beta\) cages) in which both the extraframework cations and anions are hosted (Fig. 1). The sodalites here studied are nitrite sodalite (Na\(_8\)[Al\(_6\)Si\(_6\)O\(_{24}\])(NO\(_2\))\(_2\)), nitrate sodalite (Na\(_8\)[Al\(_6\)Si\(_6\)O\(_{24}\)](NO\(_3\))\(_2\)) and a nitrite sodalite in which an O\(_2\) molecule occupies, together with a nitrite anion, one of the sodalite cages. The cell parameters of nitrite-, nitrite + O\(_2\)- and nitrate sodalite were taken from Refs. [6,8,9].

Offretite is an hexagonal zeolite, with space group \(P\bar{6}m2\). Its structure, represented in Fig. 2, comprises three type of cavities: hexagonal prism (or double 6-ring, \([4662]\)), cancrinite cages (\([4665]\)), and gmelinite cages (\([496283]\)). The unit cell [10] has two distinct tetrahedral sites namely T\(_1\) and T\(_2\): exactly 12 T\(_1\) sites, belonging to the hexagonal prism and six T\(_2\) sites, in the sixfold ring of the gmelinite cage. The adopted cell dimensions are \(a = 13.229\) and \(c = 7.338\) Å [10].

Fig. 1. Ball and stick representation of the unit cell of zeolite sodalite containing two \(\beta\) cages. Black sticks represent O atoms, gray spheres Si atoms and small gray spheres Al atoms.
We have simulated an isomorphously substituted offretite, namely titanium offretite (Ti-OFF), which was first synthesized by Kwak et al. [11]. The simulation cell contains 17 silicon atoms, one titanium, 36 oxygens and two water molecules, one inside the hexagonal prism and one inside the gmelinite cage.

These systems were studied using an advanced computational technique based on density functional theory [12,13], the ab initio molecular dynamics method of Car and Parrinello [4]. As the theoretical details of such approach have already been described in a number of papers and reviews on the subject (see e.g. Ref. [14]), here we report only the computational details needed to reproduce our results. For all the simulation runs [15], the valence electronic wavefunctions were expanded in a planewave basis set up to a kinetic energy cut-off of 60 Ry. We adopted a fictitious mass of 500 a.u. and a time step of 5 a.u. for the numerical integration of the equations of motion. Norm-conserving non-local pseudopotential [16,17] were used for Si, Ti, N, O, Na and H; the electron–electron interaction was calculated by a gradient corrected functional approximation [18,19]. The offretite simulation was performed at room temperature for a time of 3.7 ps, whereas nitrite-, nitrate- and nitrite + O₂ sodalite simulations were run at different temperatures (300 K for nitrite- and nitrate-sodalites and 400 and 1000 K for the nitrite sodalite + O₂ system), with total elapsed times in the range 2.2–4 ps.

Moreover, in order to understand the nature of the interaction between the NO₂⁻ and O₂ in the same sodalite cage we have calculated the Wannier functions for the guest species. This technique allows to obtain a set of maximally localized orbitals by a unitary transformation of the Kohn Sham orbitals [20]. The Wannier orbitals for a periodic system are the analogous of the Boys orbitals [21] for a finite system and correspond to the chemical view of molecular bonding orbitals and lone pairs.

3. Results and discussion

3.1. Nitrite- and nitrate-sodalites

The ab initio MD study of Ref. [5] established that the experimentally observed dynamical disorder of the nitrite anions in the sodalite cages is due to the rotational motion of NO₂⁻. As the time scale of such motion is of the order of about 200 fs, it is clear that
XRD experiments, which are performed on a much larger time scale (minutes), can only give an average picture of the different orientations of the guest. Thus, the disorder in the NO₂ crystallographic positions detected by XRD [6] is a consequence of the guest atomic-scale dynamical behavior. The ab initio simulation of this system can provide a reliable prediction of its crystallographic coordinates as well as a microscopic picture of the rotational behavior of the larger NO₃ anion. Inspection of the time evolution of the simulated system indicates that nitrate anions are also rotating inside the cage, even though their motion is apparently more frictioned than that of the nitrite. As the rotating nitrate anions continuously change their orientation with respect to the cage’s axes, it can be argued that, in analogy to what observed in nitrite sodalite, XRD refinements on this system should detect disorder in the NO₃ crystallographic positions.

In order to evidence and rationalize differences in the NO₂ and NO₃ rotational behavior, we have studied the time evolution of the angles φ and ψ formed by the OÑO’s bisector and by the normal to the molecular plane with the three cartesian axes. The change in time of the first set of angles (i.e. of the φ’s) provides a picture of the rotational motion of the bisector. However, the anions may also rotate around the OÑO’s bisector. It may happen that the bisector changes slightly its orientation whereas rotation occurs around the OÑO bisector. In other words, rotation of the molecular plane may take place even if the bisector keeps a fixed orientation. In these limiting cases, the behavior of the φ angles could not satisfactorily account for the presence of rotational motion. This justifies the choice of monitoring the angles φ between the bisector’s normal and the X, Y, Z axes as well.

Fig. 3 shows the angles (φ) between the OÑO bisector and the X, Y, Z axes as a function of time for nitrite and nitrate. In the latter case, only one of the three OÑO bisectors has been considered because of the D₃h symmetry predicted by our calculations for the nitrate anion (i.e. on average NO₃ is planar and the three average OÑO angles are 120°). At a first sight, the φs show a very similar trend in both nitrite and nitrate sodalite: the bisector rotates with respect to the fixed reference system on a time scale of the order of few hunredths of femtoseconds. However, while in nitrate sodalite the maximum variation of the three angles (δφ) is lower than 100°, in nitrite sodalite δφ always overcomes 150°, and reaches 180° for φₓ and φₜ, thus indicating that during the simulation time a nearly full inversion of the orientation of the OÑO bisector is observed only in nitrite sodalite.

The behavior of the ψ angles in nitrite and nitrate sodalite is shown in Fig. 4. Here, the maximum observed δψ is about 100° for NO₃ and 140° for NO₂. The difference between the maximum values of ψ calculated for the two anions is therefore lower than the difference in φ above discussed. This suggests that the rotational behavior of the normal to the plane (and therefore of the plane in which the anion lies) present stronger similarities. Such result is easily justified by remembering that both anions are planar.

On the whole, these data confirm that the nitrite anions indeed change their orientation faster than the NO₃ ones. Moreover, the larger maximum δs shown...
by NO$_2^-$ indicate that a complete inversion of the guest’s orientation is more likely to happen for the smaller NO$_2^-$ anion. We also point out that the angles’ plots here discussed are characterized by high frequency oscillations of smaller amplitude (5–10°), which may be attributed to couplings with the higher-frequency vibrational modes of the caged anions. These data therefore suggest that the motion of the confined NO$_2^-$ and NO$_3^-$ anions is a complex combination of different components (i.e. rotational, vibrational, translational and librational) rather than a pure rotational motion. Frictions due to steric factors and long-range interactions can influence the characteristic timescale of the guests’ motion. It is worth remarking that the center of mass of the guest system is also moving. Such motion should not be attributed to intercage diffusion because the requirement of charge neutrality in the β cage makes the migration of an anionic species an extremely low-probability event. Our calculations confirm this hypothesis, as no intercage diffusion event has been observed in both the studied sodalites. On the other hand, the distributions of the crystallographic coordinates of the N atoms (shown in Fig. 5) are not unimodal, indicating that in both systems the N atoms are moving about the center of the cage. Moreover, NO$_2^-$ shows wider N distributions as NO$_2^-$ occupies a smaller portion of the β cage than NO$_3^-$ and can undergo on average larger displacements. The average coordinates of the N atoms in nitrite- and nitrate-sodalite and their standard deviations calculated from the MD trajectories are reported in Table 1. The N coordinates in nitrite sodalite show larger standard deviations, in agreement with the previous discussion.
Moreover, the N atom in NO$_3^-$ is less displaced from the cage center (i.e. the (0,0,0) point in our reference system) than the N in NO$_2^2$. In fact, both the larger size and the higher symmetry of the nitrate anion favor the occupation of positions closer to the cage center.

The simulation data discussed above clearly show, that notwithstanding the close similarity of the nitrite and nitrate anions (i.e. they are both planar, have the same charge and very close chemical properties), their rotational behavior in the sodalite cage is rather different. In addition, dynamics of the caged anions is different from that of the corresponding isolated system. One of the characteristic features of interacting systems is the librational motion, which in this case arises from the confinement of NO$_2^2$ and NO$_3^-$ in the sodalite cage. The librational motion of the guest depends on the strength and the directionality of host–guest interactions, which in turn are governed by size, symmetry, and chemical composition of both the guest and the zeolitic cage. Thus, the study of librations of caged systems could provide information on some aspects of host–guest interactions in zeolites. This can be achieved by analyzing the single molecule reorientation relaxation (SMOR), defined as

$$c_1(t) = \frac{\langle \mu(t)\mu(0) \rangle}{\langle \mu(0)\mu(0) \rangle}$$  \hspace{1cm} (1)

where $\mu$ is the bisector of the OÑO angle, and a second orientational correlation function, $c_2(t)$, defined as

$$c_2(t) = \frac{\langle n(t)n(0) \rangle}{\langle n(0)n(0) \rangle}$$  \hspace{1cm} (2)

where $n$ represents the normal to $\mu$. These correlation functions were calculated for nitrite and nitrate sodalite and shown in Fig. 6. Remarkably, $c_1(t)$ and $c_2(t)$ have an oscillatory structure for both NO$_2^2$ and NO$_3^-$, thus confirming that both anions are indeed rotating [22]. However, the much lower values reached by the NO$_3^-$'s correlation functions indicate that a full reversal of orientation (i.e. a 180° rotation) is achieved only by the smaller-sized nitrite anion. Librations, which normally occur on a shorter time scale than rotations, should be responsible of the decay of the orientational correlation at short times ($\approx$0.1 ps). Since at short times both $c_1(t)$ and $c_2(t)$ decay faster in NO$_2^2$, we conclude that reorientation due to librational motion is quicker for NO$_2^2$ than for NO$_3^-$.

The characteristic frequencies of librational motion can be obtained from the Fourier analysis of the $c_1(t)$ and $c_2(t)$ correlations. If these frequencies match with those typical of some framework’s vibrational modes,

|         | NO$_2^2$-SOD | NO$_3^-$-SOD |
|---------|--------------|--------------|
| $x$ (Å) | -0.406       | -0.186       |
| $\Delta x$ (Å) | 0.325       | 0.178        |
| $y$ (Å) | -0.287       | -0.202       |
| $\Delta y$ (Å) | 0.288       | 0.188        |
| $z$ (Å) | -0.291       | -0.091       |
| $\Delta z$ (Å) | 0.207       | 0.142        |

Fig. 6. Orientational correlation functions $c_1(t)$ (bottom) and $c_2(t)$ (top) as a function of time for nitrite (thin solid line) and nitrate (thick solid line) sodalites.
it can be concluded that the librational motion of the guest system is dynamically coupled with vibrational modes of the zeolitic framework. This coupling has already been found in the case of the nitrite anion [7]. Using the same technique, we calculate the contribution of the \( \text{NO}_2^- \) librational mode to the total vibrational spectrum of \( \text{NO}_3^- \)-sodalite and compare it with that of \( \text{NO}_3^- \) in nitrite sodalite. The libration spectra of the guests and the framework’s contribution to the total vibrational spectra calculated for nitrite and nitrate sodalites are shown in Fig. 7. In both sodalites, the librational bands of highest frequencies overlap with some low-frequency framework vibrational modes in the region between 80 and 200 \( \text{cm}^{-1} \), indicating that orientational relaxation of both \( \text{NO}_3^- \) and \( \text{NO}_2^- \) is indeed coupled to the framework. This dynamical coupling seems to be stronger in nitrite-sodalite, even though the low-frequency spectra resolution is too low to draw more quantitative information. The stronger host–guest coupling found for nitrite sodalite should arise from the smaller mass (and thus lower inertia) of \( \text{NO}_2^- \) w.r.t. \( \text{NO}_3^- \), that may allow the nitrite motion to be more easily affected by the slight instantaneous changes in the host–guest interactions induced by framework’s vibrations.

These results are also supported by the good agreement of the calculated vibrational frequencies of the caged \( \text{NO}_3^- \) and \( \text{NO}_2^- \) with the experimental IR spectra of nitrite and nitrate sodalite [23]. The vibrational spectra calculated from the FT of the \( \text{NO}_3^- \) and \( \text{NO}_2^- \) velocity autocorrelation functions are shown in Fig. 8. The N–O stretching frequency of \( \text{NO}_3^- \) (1340 \( \text{cm}^{-1} \)) and \( \text{NO}_2^- \) (1220 \( \text{cm}^{-1} \)) well compare with the corresponding experimental ones (1390 and 1270 \( \text{cm}^{-1} \)), in particular the nitrite/nitrate frequency shift is in very good agreement with experiment. The discrepancy of 50 \( \text{cm}^{-1} \) between absolute frequency values is a well-known effect due to the use of fictitious masses in Car–Parrinello simulations [24].

3.2. Nitrite + \( \text{O}_2 \)-sodalites

We have shown that two caged anions characterized by only slight differences have indeed a different rotational behavior owing, among other factors, to their different host–guest interactions. In this section
we examine how the guest–guest interactions affect rotational motion by studying a nitrite sodalite with one oxygen molecule per unit cell. The O$_2$ occupies one of the two β cages in the unit cell, thus interacting at short range with the NO$_2$ anion already present in this cage (cage A from now on). As intercage diffusion of the O$_2$ was never observed in our simulation, in the second β cage (cage B from now on) only a NO$_2$ anion is included, whose rotational behavior should closely resemble the one shown by NO$_2$ in nitrite sodalite. Comparison of the motion of the nitrite anions in cage A and cage B may provide some insight into the changes brought about by an increased concentration of guest species. Moreover, ab initio simulations of this system were performed at two different temperatures (400 and 1000 K) so as to study the effect of temperature on the guest’s motion.

The angles ϕ and ψ were calculated as a function of time for the two NO$_2$ in cage A and in cage B. As expected, at a simulation temperature of 400 K the time variation of both ϕ and ψ for the NO$_2$ in cage B (not shown) is very close to that found in nitrite sodalite, whereas the plots of ϕ and ψ for the NO$_2$ in cage A (Fig. 9) clearly indicate a different rotational behavior for the NO$_2$ interacting with the O$_2$. While the maximum δϕ for NO$_2$(A) is 150° as in nitrite sodalite, oscillations of the ϕ angle are characterized by a much smaller amplitude, being the maximum δϕ only 50°. This suggests that the rotation of NO$_2$(A) is, in general, more frictioned than NO$_2$(B). In particular, the small value of δϕ$_{max}$ for NO$_2$(A) indicates that a complete rotation of the ONO bisector never occurs. Such hindered motion may be safely attributed to the co-presence of the oxygen molecule in the cage, which restricts the empty space available to NO$_2$(A). On the other hand, the very similar behavior of the angle ψ (i.e. very large values of δψ) shown by NO$_2$(A) and NO$_2$(B) indicates that the NO$_2$(A) is still rotating without additional frictions around the ONO bisector. In other words, the effect of the presence of an additional guest in cage A on the NO$_2$ rotational motion is to introduce a preferential rotation axis, which could be identified with the ONO bisector. This implies that the O$_2$–NO$_2$(A) guest–guest interaction occurs along a preferential direction. It is worth remarking that the above discussed behavior of the ϕ and ψ angles of NO$_2$(A) does not change qualitatively with increasing temperature. Owing to the higher thermal excitation, larger maximum values of δϕ and δψ are found at 1000 K (161 and 95° for δϕ and δψ, respectively). However, ϕ and ψ keep on having a different behavior also at 1000 K, indicating that rotational friction arising from the directional guest–guest interaction is strong enough to survive even in a high-temperature regime. Since at 1000 K the thermal energy is 2.0 kcal/mol, we deduce that the O$_2$–NO$_2$ interaction energy should be at least of this order of magnitude. It would be interesting to have a deeper insight into the chemical nature of such interaction.

Our results indicate that during the sampled evolution time the nitrite anion is indeed constantly connected to the oxygen: the O–O bond and the ONO bisector form an unique axis, along which rotation occurs. Thus, the two guests in cage A, O$_2$ and NO$_2$,
are no longer two rotationally independent systems but behave as a single $O – O – NO_2$ anion owing to the strong short-range $O – N$ interaction. The Wannier orbitals localized on $O – O – NO_2$ have been calculated [25]. The Wannier orbitals localized on $O – O$, represented in Fig. 10a, differ very little from the molecular orbitals of an isolated $O_2$ molecule. In particular, both the $\sigma$ and $\pi$ $O – O$ bonding orbitals are present, indicating that interaction with the nitrite anion is not strong enough to induce a significant perturbation of the $O_2$ electronic structure. Therefore, no new $N – O$ covalent bond between the two guests is formed. On the other hand, $NO_2^-$ with its negative charge should be a rather strong Lewis base and might act as a donor of electrons towards $O_2$. Such hypothesis is confirmed by the inspection of the Wannier orbitals localized on the nitrite. One of these orbitals, shown in Fig. 10b, is mainly localized on a $N – O$ bond, but a significant portion of its electronic density is concentrated in the region of the guest–guest $N – O$ bond. This density shift along the $N – O$ direction has the effect of holding together the two guests, thus altering their rotational behavior without affecting significantly their chemical nature. In conclusion, our analysis of the guests’ electronic structure has allowed us to establish the nature of the $O_2 – NO_2$ interaction and its effect on rotations. No chemical reaction between the two guest systems occurs, and the partial charge transfer from $NO_2^-$ does not lead to the activation of molecular oxygen.

3.3. Water molecules in Ti-offretite

Ti-offretite contains one water molecule inside the hexagonal prism ($H_2O$ A) and one inside the gmelinite cage ($H_2O$ B). Owing to the chemical composition of the framework, that does not contain any aluminum atom, the Ti-OFF cages are hydrophobic suggesting that water molecules should be located on average in the proximity of the cage’s centers. The two $H_2O$ in the unit cell occupy cages of different dimensions, so that the motion of water molecules in different environments can be studied. Fig. 2 clearly shows that the dimensions of the gmelinite cage are large enough to allow $H_2O$ to rotate rather freely, whereas the small size of the hexagonal prism suggests that the $H_2O$’s rotational motion might be strongly hindered by formation of host–guest hydrogen bonds. In our simulation $H_2O(B)$ occupies an average position close to the gmelinite cage’s center. Moreover, no hydrogen bond is formed with framework oxygens, indicating that the rotational behavior of $H_2O(B)$ is governed only by long-range host–guest interactions. On the other hand, the rotation of $H_2O(A)$ is heavily frictioned by the presence of water-framework.

![Fig. 10. Representation of the $O_2 – NO_2$ (A) structure and Wannier orbitals. White spheres represent O atoms; the gray sphere represents the N atom. (a) Contour plot of the Wannier orbitals localized on $O_2$. (b) Contour plot of a Wannier orbital partially localized along the guest–guest $N – O$ bond.](image-url)
hydrogen bonds, i.e. by strong short-range host–guest interactions.

The calculated average distances of the H atoms in H$_2$O(A) from the oxygen atoms of the hexagonal prism are in the range 2–3 Å, confirming that water-framework hydrogen bonds are indeed present, but they are continuously broken and re-formed during the simulation time. In fact, analysis of the H⋯O$_{\text{framework}}$ distances vs. time shows that the H atoms are changing the framework oxygen atoms to which they are hydrogen bonded. Thus, the availability of more framework oxygen atoms at short enough distances allows the water molecule to change its orientation inside the prism in search of different hydrogen-bonding partners. As the breaking of an hydrogen bond has a non-zero energy cost, rotation of H$_2$O(A) should be much more hindered in comparison to that shown by the water molecule in the larger mordenite cage.

A closer inspection of the rotational behavior of the two water molecules has been performed by calculating the angles $\phi$ and $\psi$ defined in the previous sections. Only the plots of the $\phi$ angles vs. time are shown in Fig. 11, as the trends of $\phi$ and $\psi$ are very similar. It is clear that H$_2$O(B) undergoes rather unfrictioned rotations, as its orientation with respect to the crystallographic axes abruptly changes on a time scale of the order of 200 fs. Both $\phi$ and $\psi$ have maximum spreads of about 180°, pointing to a complete reversal of the molecule’s orientation around both the HÖH bisector and its normal. Much different is the behavior of the $\phi$ and $\psi$ angles for the water molecule hosted in the smaller hexagonal prism. A complete reorientation of H$_2$O(A) never occurs in the simulation time. In particular, the small maximum spread shown by the H$_2$O(A)’s $\phi$ angles (30°) indicates that the rotational motion of the HÖH bisector is heavily frictioned, owing to the above-discussed breaking and reforming of water-framework hydrogen bonds. On the whole, the trend of both $\psi$ and $\phi$ suggests that the motion of H$_2$O(A) should be more properly considered as mainly librational rather than rotational. Further insight on this issue can be obtained by comparing the reorientational relaxation functions $c_1(t)$ of H$_2$O(A) and H$_2$O(B) shown in Fig. 12. While the H$_2$O(B)’s $c_1(t)$ presents the oscillatory behavior
typical of an almost freely rotating system, the one of H$_2$O(A) has a more complex structure, indicating that other kinds of motions (in this case, librational motions) are the main responsible of H$_2$O(A) reorientations. This is also proven by the behavior of $c_1(t)$ at short times, which is in general determined by quick librations. Remarkably, the H$_2$O(B)’s $c_1(t)$ has a shoulder at about 0.02 ps indicating that also the dynamical behavior of the water molecule in the larger cage has a partial librational character. However, the orientational correlation decays faster in H$_2$O(A) because of its quicker librational motion, which may be due to a stronger coupling to the framework’s dynamics. This hypothesis can be verified by comparing the Fourier transform of $c_1(t)$ of the two water molecules with the vibrational spectrum of the offretite framework (Fig. 13). In agreement with the previous discussion, the libration spectra of both water molecules show non-zero absorptions which are superimposed to some low-frequency framework vibrational modes. In addition, while the H$_2$O(B)’s libration spectrum dies off at frequencies of about 260 cm$^{-1}$, that of H$_2$O(A) shows finite intensities in a much larger frequencies range (up to 500 cm$^{-1}$). This proves that the librations of the water molecule in the hexagonal cage are actually coupled to a larger number of framework’s modes owing to the presence of strong short-range host–guest interactions. These interactions heavily hinder H$_2$O(A) rotations and prevent a complete molecular reorientation, but at the same time are responsible of its faster librational motions. As a global result, H$_2$O(A) changes its orientation less but quicker than H$_2$O(B) because reorientation is mainly governed by librations in the former case and by rotations in the latter.

4. Summary and conclusions

The rotational motion of different guest species hosted in zeolitic cavities of varying size has been investigated in the simulation work here presented. In particular, we have addressed the question of establishing up to what extent interactions with the framework and with other guests may change the dynamics of the confined species with respect to that of the corresponding isolated system. Our results show that it is not possible to predict the rotational behavior of a caged system simply on the basis of the relative dimensions of the zeolitic cage and of the guest species. Moreover, confined species actually show a combination of different types of motions. The dominant character of the guest’s motion and its characteristic timescale are determined by a complex balancing of different factors depending on the size, the physico-chemical properties and the concentration of the guest systems as well as on the size, structure and chemical composition of the framework. We notice here that in our simulated systems all rotations occur in a continuous way and sudden rotational jumps have not been observed.

Our final conclusion is that there is no simple and general correlation between framework or guest properties and the motion of the caged system. The reason is that the dynamics of the guest is indeed determined by its interactions (either with the framework or other caged species) and, as shown by our results, can be deeply influenced by only slight changes of these interactions. Thus, a detailed knowledge of the dynamical behavior of a given species confined into a zeolitic cage could be obtained only by an accurate, atomic-level study of the specific framework + guest ‘supersystem’.

Fig. 13. Calculated contributions to the total vibrational spectrum of $c_1(t)$ for H$_2$O(A) (dashed line), $c_1(t)$ for H$_2$O(B) (thin solid line) and of the framework’s modes (thick solid line). Intensity is in arbitrary units.
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