Computer simulations of nitrogen-containing molecular systems at very high density
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7

The dynamics of doubly occupied $N_2$ clathrate hydrates

7.1 Introduction

Clathrate hydrates form a crystalline ice-like hydrogen-bonded network composed of cavities [Rip94, Slo90, Atw91]. Guest molecules are located inside these cavities (or cages), although not all of the cages need to be occupied to form a stable lattice. Clathrate hydrates with $N_2$ molecules as guests form clathrate structure II [Dav84, Dav86]. The unit cell contains 136 water molecules, forming 16 small (radius 3.9 Å) and 8 large (radius 4.7 Å) cavities.

Experimental results [vH93, vH94, Cha97, Kuh97, Pau99, Pau97, Cha98] suggest the existence of a partial double occupation of the large cages. This is an unexpected phenomenon, considering the size of the $N_2$ molecule (about 3.6 Å). We have reported earlier molecular dynamics (MD) results on the stability ([vK01], chapter 5) and properties ([vKacc], chapter 6) of a model system of $N_2$ clathrate hydrates. In the MD simulations a doubly occupied structure II $N_2$ clathrate turned out to be stable for all the pressures, temperatures and compositions at which the simulations have been performed. The structure of the host lattice is very similar to that of a singly occupied clathrate hydrate. The behaviour of basic thermodynamic quantities is completely analogous to, and of the same order of magnitude as in the case of single occupations. For instance, the clathrate–amorphous transition appears at about the same pressure for singly as for doubly occupied clathrates. We have also compared the coherent neutron diffraction and Raman spectrum for the case of doubly occupied clathrates with those of the singly occupied clathrates and with experimental results.

The results in chapter 5 and 6 did not include an analysis of the dynamic behaviour. In this paper we investigate the dynamics by a study of the translations and reorientations (phonons and librations). An analysis of the time dependence of various quantities is of interest not only because it provides insight into the system, but also because the dynamical properties may be related to experimental results: in addition to the existing data, there is a need for additional experimental evidence for the existence of (partial) doubly occupied clathrates. With the MD results, one can make predictions about possible experimental
results, thus facilitating their interpretation. Therefore, we present dynamical properties of the doubly occupied clathrate and compare it with the case of single occupation. These properties also lead to new insight in the behaviour of a doubly occupied clathrate.

In particular, we calculate the intermolecular vibrational density of states (DOS), the mean square displacements (MSDs) and the reorientational autocorrelation functions (re-orientational ACFs). Several computer simulation studies [Ino96, Tan94, Tan93b, Tan93a, Tse87, Tse84, Tse83] have dealt with similar dynamical properties, but only for single occupations. In this work we study doubly occupied clathrates with N\textsubscript{2} guest molecules. These are the only molecules for which double occupancy has been observed [Kuh97]. For comparison, we also perform simulations with single occupancies. As a spin-off, these results complement previous studies of singly occupied clathrate hydrates, since only a limited study included results for N\textsubscript{2} guests [Hor97b]. Where appropriate we compare previously obtained results with the results presented in this paper.

7.2 Simulation details and potential models

Classical molecular dynamics simulations were employed, for which the DL_POLY package [DLP98] has been used. In addition, a number of analysis programs were written. Constant pressure as well as constant volume simulations were conducted. Details of the simulation techniques and methods used can be found in chapter 5 and Refs. [A1186, Fre96, DLP98]. The simulation cell consisted of 8 unit cells, corresponding with 128 small and 64 large cages. The initial positions of the O atoms were deduced from x-ray diffraction experiments [Mak64] and the positions of the H atoms were randomly selected while obeying the Bernal-Fowler ice rules [Ber33]. The molecules were modelled as having no internal degrees of freedom. The water molecule consisted of one van der Waals interacting site and three point charges to represent the water dipole moment (SPC/E model, Ref. [Ber87]). The nitrogen molecule contained two van der Waals interacting atom sites. Four point charges were added to represent the molecule’s quadrupole moment [Buc68]. The cages to be filled, being either in single or double (large cages only) occupation were selected at random, as was the initial orientation of the N\textsubscript{2} molecules. The total number of guest molecules in the small cages is indicated with \( N_{S,S} \) (single occupancy only: \( N_{S,S} \leq 128 \) for 8 unit cells). Likewise, the number of guest molecules in the large cages are \( N_{L,S} \) and \( N_{L,D} \) for single and double occupancy, respectively (\( N_{L,S} \leq 64, N_{L,D} \leq 128 \)). In the calculations, a pressure of 1 kbar and temperatures of 80 and 273 K were maintained. Unless indicated otherwise, the 50% of the large cages were doubly occupied (\( N_{S,S} = 128, N_{L,S} = 32, N_{L,D} = 64 \)), unless indicated otherwise. Although \((N, V, E)\) simulations are the preferred way to calculate the dynamical properties [Fre96], we have calculated the dynamics directly in the \((N, p, T)\) simulations. Previously it was found that the influence of the heat bath-coupling on the dynamics was only small [Tan93b]. In \((N, p, T)\) simulations, it is more likely that the system will reveal instabilities. For instance, the absence of a constant (flat) asymptotic MSD value would indicate a long time drift of the water molecules.

In MD simulations, the vibrational density of states (DOS) can be obtained from the
Fourier transform of the velocity ACF [Esb73, Dic69]:

\[
z(\omega) = \int_0^\infty e^{-i\omega t} \langle \mathbf{v}(t') \cdot \mathbf{v}(t' + t) \rangle \, dt.
\]  

(7.1)

where \( \mathbf{v}(t) \) is the velocity of a particle at time \( t \), and \( \omega \) is the frequency. The brackets denote averages over the number of molecules and time origins \( t' \). We calculated this quantity for rigid molecules, therefore the spectra include the translational modes (phonons) as well as rotational modes (librons) of the molecules. The obtained distributions are single particle functions. However, in general the atomic displacements are a superposition of the single-particle diffusive motions and the collective normal mode oscillations. Thus, the Fourier components of the velocity ACF of rigid molecules contain information on the phonon and libron density of states.

The center-of-mass (CM) of the water molecule nearly coincides with the position of the O atom. Therefore, the translational or phonon modes are dominated by the motions of the O atoms: the rotational or libron modes are dominated by the H atoms [Wha73, Wha67]. For the N\(_2\) guest molecules we have calculated the power spectra of the motions of the N atoms and of the molecular mass centers. The CM motions are related with translational modes only. Assuming complete decoupling of the translational and rotational motions, the presented spectra for the CM motions may be representative for monoatomic guest molecules of similar size and interaction. The motions of the N atoms contain translational as well as rotational contributions. The results may be compared with (future) experimental results, since the vibrational density of states can be determined by incoherent inelastic neutron scattering and spectroscopic methods.

An indication of the vibrational amplitude of the atomic or CM motions can be obtained from the mean squared displacements (MSDs):

\[
m(t) = \langle |\mathbf{r}(t' + t) - \mathbf{r}(t')|^2 \rangle.
\]  

(7.2)

with \( \mathbf{r} \) the position of the atom or of the CM. The MSDs as a function of time also provide more insight into the dynamic behaviour itself.

Whether or not the rotations are hindered, and to what extent this is the case for the different types of filling, may be obtained by a study of the reorientational ACFs. The reorientational behaviour of the guest molecules is investigated by the calculation of the single particle ACF

\[
C_1 = \langle P_l(\cos(\theta(t))) \rangle = \langle P_l(\mathbf{n}(t') \cdot \mathbf{n}(t' + t)) \rangle.
\]  

(7.3)

where \( P_l \) is the \( l^{th} \) order Legendre polynomial and \( \theta(t) \) is the angle between the \( N_2 \) bond axis \( \mathbf{n} \) at time \( t' \) and time \( t' + t \). We have calculated \( C_1 \) and \( C_2 \). In general, the molecules rotate freely at short times (\( C_1 = e^{-\frac{lt^2}{\langle I \rangle}} \), with \( I \) the molecular moment of inertia), while for long times, Debye small step rotational diffusion occurs (\( C_1 = e^{-\frac{lt}{D \langle I \rangle^2}} \), with \( D \) the rotational diffusion constant) [Til83, Boh84]. The shapes of the infrared and Raman bands and the relaxation times measured by NMR are related with \( C_1 \) and \( C_2 \) [Til83, Boh84]. For nonpolar molecules, \( C_1 \) has no experimental significance, but in the MD calculations it provides direct insight into the reorientational behaviour. \( C_2 \) represents
7. The dynamics of doubly occupied N\(_2\) clathrate hydrates

Figure 7.1: Calculated power spectra at 80 K, associated with the motion of the water molecules, for case I (a), II (b) and III (c): O atoms (solid line) and H atoms (dashed line). Due the truncation of the velocity ACF, its Fourier transform has spurious ripples of nearly equal energy spacing [Dic69].

the time dependence of the anisotropy of the molecular polarizibility. In experiments, the depolarized component of the scattered radiation can be written in terms of \(C_2\). This component corresponds to rotational Raman scattering if the vibrational states are unchanged. Moreover, it corresponds to the anisotropic part of the vibrational band in the case of the vibrational Raman effect. For example, for liquid N\(_2\), the Fourier transform of \(C_2\) is related with the rotational side bands in the Raman scattering spectrum [Bar73, Chu75, Chu76].

7.3 Results and discussion

7.3.1 Intermolecular vibrational density of states

To investigate unambiguously the influence on the dynamics of the host lattice by the three different types of filling, we have calculated \(z(\omega)\) for three hypothetical cases: \(N_{L,S} = N_{L,D} = 0, N_{S,S} = 128\) (case I), \(N_{S,S} = N_{L,D} = 0, N_{L,S} = 64\) (case II) and \(N_{S,S} = N_{L,S} = 0, N_{L,D} = 128\) (case III). Figure 7.1 shows the results at 80 K and 1 kbar.
We first discuss the general features that appear in the three calculated spectra. A frequency gap between 350 and 525 cm\(^{-1}\) between the phonon modes (O atom motions) and libron modes (H atom motions) is clearly present. Roughly speaking, the translational band consists of three branches: a low frequency branch with a maximum at about 75 cm\(^{-1}\), followed by an intensity dip around 120 cm\(^{-1}\) and two less intense branches around 200 and 300 cm\(^{-1}\), respectively. The region below and above the dip at 120 cm\(^{-1}\) correspond to acoustic and optic vibrations, respectively [Ino96, Tse87]. The libron band sharply rises at around 525 cm\(^{-1}\), reaching a maximum close to 575 cm\(^{-1}\). A dip at 620 cm\(^{-1}\) and a second peak near 630 cm\(^{-1}\) follow. After the second peak, an almost linear decrease down to 1100 cm\(^{-1}\) occurs, although in this range roughly three overlapping branches around 700, 850 and 1000 cm\(^{-1}\) may be discriminated. The results are in correspondence with those obtained earlier for single fillings [Ino96, Tan93b, Tse87, Tse84].

Upon a double filling of the large cages, the optic branch of the phonon band shows a slight shift to smaller frequencies. As a result, the intensity dip at 235 cm\(^{-1}\) for both case I and case II, has shifted to 225 cm\(^{-1}\) for case III and it is less deep. For the libron band, an intensity decrease of the two main peaks (at 575 and 675 cm\(^{-1}\)) is accompanied by a small shift to lower frequencies as compared to case I and II. The shifts of both the optic phonon branch and the libron band may indicate a weakening of the H-bonds.

A frequency decrease of the acoustic phonon band, as illustrated by the peak at 40 cm\(^{-1}\), is observed for case II only. In fact, the vibrational DOS for an empty host lattice (not shown) is very similar to that of case II. The frequency lowering of in this case the acoustic branch suggests a weakening of the host lattice. This corresponds with the intuitive idea that in that case a water molecule can spend a relatively large amount of time away from its equilibrium position before colliding with a guest molecule. In this picture, we may assert that filling the small cages substantially increases the rigidity of the host lattice. These guests provide an excluded volume that damps out those lattice modes that lead to an instability of the host lattice [Rod90]. Double occupancy of the large cages also provides some support to the host lattice, albeit smaller than in the case of a filling of the small cages. Thus, in this reasoning, for a single occupation of the large cages the host lattice is less stable than for double occupation.

The results for the guest molecules ('rattling phonons' [Nol99]) are shown in Fig. 7.2. We first focus on the single fillings. For the CM motions, one peak is observed in both the small (near 66 cm\(^{-1}\)) and the large (near 20 cm\(^{-1}\)) cages. The smaller void space in the small cages results in an increased hindrance of the guest translational motions as compared to the large cages, leading to a lower frequency for the latter. Also, the peak width is smaller in that case. In the spectrum of the N atoms, the rotational modes are superimposed on the translational modes. The latter dominate the N atom spectrum. For the small and large cages, an intensity increase on the low and high frequency side of the CM peaks occur, respectively. As for the host lattice, our results for the guest molecules are similar to those in other reports [Ino96, Tse87, Tse84].

For the double fillings, the dynamics of the guest molecules are clearly different: a broad band between 0 and 200 cm\(^{-1}\) occurs, which consists roughly of two branches near 45 and 145 cm\(^{-1}\). Moreover, a peak near 21 cm\(^{-1}\), and a wing near 77 cm\(^{-1}\) can be discriminated. This spectrum is in contrast with the relatively narrow peaks for single fillings. The complex spectrum, in particular the peaks at 45 and 145 cm\(^{-1}\), possibly
results from two different motions in different local environments. The peak at 20 cm\(^{-1}\), at which the large cages in single occupation reveal the only peak, suggests a similar translational component for both cases. Frequencies around 145 cm\(^{-1}\) are only present for double fillings, this branch is possibly related to the enhanced hindrance due to the smaller void space. For the N atom motions, increased intensities near 24 and 110 cm\(^{-1}\) are observed.

The appearance of a broad frequency range, including a peak at 145 cm\(^{-1}\) are unique to the molecules in the doubly occupied cages. In principle, if in experiments a sufficient amount of large cages contain pairs of molecules, a similar spectrum should be obtained.

In addition, we have calculated the vibrational DOS at 273 K (not shown). For the host lattice, there is a shift of both the phonon and libron band to lower frequencies for all three cases, obviously related to the thermal expansion. In contrast, a shift to higher frequencies occurs for the guest molecules, a consequence of the increased thermal velocities of the weakly bound guests. These temperature dependencies have been observed in previous reports [Tan93b, Ino96]. For the double fillings, the two peaks found at 80 K (Fig.7.2(c)) broaden to such an extent that one broad, highly asymmetric peak results.

### 7.3.2 Mean squared displacements

Figure 7.3 shows the MSDs for the various types of atoms as a function of simulation time at 273 K. For all atoms, the behaviour is typical that of a solid: there is an oscillatory relaxation to a long-time, constant (horizontal) asymptotic value. Due to decreasing statistics, the fluctuations in the curves increase as a function of time.

The O atoms have an asymptotic value of 0.35 Å\(^2\), which is close to the values found in previous works [Hor97b, Tan93b, Rod90]. The MSD-vs-time behaviour of the H atoms is practically the same as that of the O atoms, apart from a small upward shift of the curve.
Figure 7.3: The MSDs at 273 K as a function of time for the various atoms in the system. The water molecules are indicated by the open symbols (on this scale, the MSDs for the O and H atoms overlap). The guest molecules are denoted by the solid (CMs) and dashed (N atoms) lines. Indicated are the N₂ molecules in the small, singly occupied large and doubly occupied large cages, respectively, with increasing line thickness (the CM motions of the guests in the small cages for the greater part overlap with that of the water molecules). For detailed simulation conditions, see text.

Due to the librational motion of the water molecules; the asymptotic value is 0.37 Å². The asymptotic behaviour endorses the result that the doubly occupied clathrate is stable. For the guest molecules, the asymptotic values for the CMs in the small, singly occupied large and doubly occupied large cages are 0.41, 2.0 and 5.5 Å². As for the water molecules, the course of the N atoms is very similar to that of the CMs. In this case, the upward shift due to the rotations is 0.6 Å².

Of course, the guest displacements in singly occupied large cages are much larger than for the (singly occupied) small cages. The result that the MSDs for the doubly occupied large cages are largest is counter-intuitive since in that case the available void space is smaller. However, the result indicates that the presence of the N₂ neighbour does not prevent a N₂ molecule from displacing through the large cage. The results correspond with the distances of the guest molecules to the center of the cage (chapter 5): these are 0.22, 0.85 and 1.6 Å for the N₂ molecules in the small, singly occupied large and doubly occupied large cages, respectively. The characteristic equilibration time of the MSD curve is a measure for the rate with which the molecules move through the cage. This is the largest for double occupations, as expected from the presence of the neighbouring N₂ molecule.

Support of the suggestion that each individual N₂ molecule diffuses through the whole cage is obtained from a plot of the trajectories of the CMs of the guest molecules. Fig 7.4 shows the trajectories for four guest molecules within three selected cages. These three
cages were selected at random; other cages show similar behaviour. The trajectories are consistent with the MSD plots (Fig 7.3). For the double fillings, each N\textsubscript{2} molecule spends a relatively large amount of time at each of two locations. These locations correspond with local energy minima. However, each guest also spends some time inbetween these energy minima. Both molecules migrate between their energy minima simultaneously. This picture supports the idea of a rotating pair of N\textsubscript{2} molecules. It is consistent with the relatively long MSD equilibration time that the molecules spend a relatively large amount of time in the local energy minimum and only occasionally migrate from one local energy minimum to the other. The two kinds of motions may correspond with the two components in the vibrational spectrum (Fig 7.2(c)). Although Fig. 7.4 only shows two energy minima, it is likely that the energy minima are related with the four hexagons that are present within the wall of the large cage. In an x-ray diffraction study it was shown that the density distribution of the molecules in the large cages of air hydrates have four maxima displaced from the center [Hon90].

### 7.3.3 Reorientational motion

Figure 7.5 shows C\textsubscript{1} and C\textsubscript{2} at 80 K. The general behaviour is as follows. The gaussian behaviour indicates that the molecules behave as free rotators at very short times, which is roughly followed by a (exponential) decay at medium times. An oscillation around a slowly decaying or constant value follows. The results for the pure nitrogen fluid, shown for comparison, are in agreement with previous results [Bar73, Chu75, Chu76]

For t > 1 ps, C\textsubscript{1} shows a slow decay for the small and double fillings, the correlations being larger in the latter case at all times. In contrast, correlations are absent for a single filling of the large cages, as C\textsubscript{1} oscillates around zero. For t > 10 ps (not shown), this is the case for all fillings.

Absence of long time correlations for a single filling of the large cages occurs not only for C\textsubscript{1}, but also for C\textsubscript{2}. For the guests in the small cages, C\textsubscript{1} > 0 in the ps range corresponds with a constant non-zero value of C\textsubscript{2}; for t > 10 ps it is still constant. Even though C\textsubscript{1} is largest for double fillings, it corresponds with a very slow decay of C\textsubscript{2}, which is continued for t > 10 ps (but is non-zero up to 40 ps).

Compared to the fluid, in the ps range, the C\textsubscript{1} correlations are smaller in the singly occupied large cages: its behaviour is comparable with that of the classical free rotator. This is undoubtedly due to the dimensions of the large cage, as a result of which the molecular reorientations are less hindered. The collision time of these guest molecules, as obtained from the peak of the vibrational DOS (Fig. 7.2(b)), is 1.7 ps. This is clearly larger than the C\textsubscript{1} and C\textsubscript{2} correlation times as estimated from Fig. 7.5 (0.3 and 0.2 ps, respectively), consistent with the idea of free rotation for the guests in the singly filled large cages. This effect is overruled by the high local density for double occupation. Roughly speaking, the orientational correlations persist longer as the available void space decreases: it is increasingly difficult for a N\textsubscript{2} molecule to lose its orientation due to the collisions with its surroundings. This is illustrated by the slow decay in C\textsubscript{1} and the very slow decay in C\textsubscript{2}.

The slow decay in C\textsubscript{1} is not unique to double fillings, as it is also observed for the small cages. However, the very slow decay in C\textsubscript{2} observed at longer times is a property of the
Figures 7.4: The trajectories of molecules in randomly selected cages at 273 K. The open circles denote the positions of the mass-centers of the N₂ molecules with time-intervals of 0.1 ps, the lines connect subsequent positions. Shown are trajectories for molecules in a small (a), singly occupied large (d) and doubly occupied large (c,d) cage: (c) and (d) are the trajectories of the corresponding pair of molecules in the same large cage. The closed dot denotes the center of the cage (obscured by the trajectories in case (a)). For all axes, the difference between the maximum and minimum value is 4 Å. Note that the distance between the positions is an estimate for the velocity. For detailed simulation conditions, see text.

guests in the doubly occupied cages only. This corresponds to an increased intensity of the low-frequency components. For the small cages, the $C_2$ long-time value is constant. This indicates that the guest molecules exhibit orientational preferences in the small cages. We expect this order to be local. An orientational order does not occur for the singly filled large cages, while the slow decay in $C_2$ suggests the same for the doubly occupied large cages. The behaviour at 273 K (not shown) is similar, obviously with correlation times much shorter than at 80 K. Also, the decreased long-time value of $C_2$ in the small cages indicates that the orientational preference decreases with temperature.
In chapter 5, we have determined the orientational correlations of the two molecules in the doubly occupied cages by a calculation of the (pair) distribution \( p(\cos(\theta_{ij})) \), where \( \theta_{ij} \) is the relative angle between molecules \( i \) and \( j \). The molecules turn out to have a preference to be aligned, this alignment being caused by the \( \text{N}_2-\text{H}_2\text{O} \) van der Waals interaction. Considering the tetrahedral symmetry of the large cage, this was an unexpected result. Therefore, it seems worthwhile to investigate this further by calculating the ACF

\[
C'_l(t) = \langle P_l(\cos(\theta_{ij}(t'))) \rangle P_l(\cos(\theta_{ij}(t + t'))) \rangle. \tag{7.4}
\]

These functions provide information on the persistence of the alignment; again we have calculated the functions for \( l = 1 \) and \( l = 2 \). The results are shown in Fig. 7.6. These correlation functions behave in a very similar manner as \( C_1 \) and \( C_2 \), with similar timescales. \( C'_1 \) shows a slow decay. In contrast, there is still a long-time correlation for \( C_2 \), even for \( t > 10 \) ps (not shown): the (‘quadrupolar’) alignment of the two molecules is long-lasting, although the (‘dipolar’) relative orientations change from parallel to antiparallel.
Figure 7.6: The autocorrelation functions $C_1'$ (see text), for $l = 1$ (a) and 2 (b), at 80 K. Shown are the results for double occupancy (the pairs of molecules in the large cages, line) and for arbitrary pairs in the fluid (open squares). The scatter increases with time.

The figure also shows the results for the N$_2$ fluid. In that case, the N$_2$ molecules are distributed homogeneously, and the assignment of pairs of molecules is arbitrary; the orientations of such pairs of molecules are uncorrelated. The short-time behaviour of $C_2'$ is the same as in the clathrate. In contrast, there are no long time correlations in the fluid, while such correlations are present in the doubly occupied clathrate, in particular for $C_2'$.

Hardly any decay in its long-time behaviour can be observed (up to 40 ps).

We conclude that the alignment of the two molecules is a long-lasting phenomenon. The change from ‘parallel’ to ‘antiparallel’ is obviously a result of the reorientations of the molecules, which explains the similar behaviour of $C_1'$ and $C_1$ for the double fillings.
7.4 Conclusions

When going from single to double occupancies, the vibrational DOS of the guest molecules show the most distinct changes. We obtain narrow, symmetric peaks at 20 and 66 cm\(^{-1}\) for the singly filled large and small cages, respectively. In contrast, for double fillings a broad range of frequencies occurs, consisting roughly of two peaks at 45 and 145 cm\(^{-1}\). These differences are expected to represent the most unique characteristic spectral feature of double occupancy. However, experimentally it may not be trivial to discriminate between the response from the guest and the host molecules. This is in particular the case for incoherent neutron scattering as the cross section of the N atoms is much smaller than for the H (or, alternatively, D) atoms. Therefore, the changes found for the host lattice, although more subtle than for the guest molecules, are important from an experimental point of view. For double occupancy, the libron band and the optic phonon branch shift to smaller frequencies, as compared to single fillings. On the other hand, for the acoustic phonon branch, there is no difference with a filling of the small cages; instead this branch shift to smaller frequencies upon a single filling of the large cages.

There is a significant translational diffusion of the N\(_2\) molecules in the cages. Despite the high local density, the thermal motions are in particular large for the doubly occupied cages. Although the two N\(_2\) molecules spend a relatively large amount of time at local energy minima separated by a distance of 3.2 Å, they migrate simultaneously to other local energy minima. The two motions possibly correspond with the two peaks found in the vibrational DOS for double fillings.

The N\(_2\) molecules in the small cages are, at least locally, orientationally ordered. For single fillings, the molecules in the large cages behave similar to a free rotator. For double fillings, the orientational correlations show a very slow decay at long times. The alignment of the two molecules in the large cages is a long lasting phenomenon, although the relative orientations change on the ps time scale.