A first principles molecular dynamics study of vibrational spectral diffusion and hydrogen bond dynamics in liquid methanol

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Abstract

We present a first principles theoretical study of vibrational spectral diffusion and hydrogen bond dynamics in liquid methanol at room temperature. The dynamics of spectral diffusion of OD modes of deuterated methanol reveals two times scales: a short time scale of about 120 fs and a longer time scale of about 3.2 ps. A damped oscillation is also found at around 120–180 fs. Calculations of power spectrum of relative velocities and hydrogen bond correlation functions reveal that the short time dynamics originates from intermolecular motion of hydrogen bonded methanol pairs while the long time relaxation corresponds to the breaking dynamics of hydrogen bonds. The quantitative details of the time constants are found to depend on the frequency of tagged OD bonds.

1. Introduction

Methanol is the simplest organic molecule containing both hydrophilic (hydroxyl) and hydrophobic (methyl) groups. The structure of liquid methanol has been extensively studied using neutron and X-ray diffraction and spectroscopic methods [1–8] and also theoretically [9–16]. Due to the presence of hydroxyl group, methanol molecules form hydrogen bonds which greatly influence the characteristics of this solvent. However, unlike liquid water where each molecule forms about four hydrogen bonds [17,18], each molecule in liquid methanol forms only about two hydrogen bonds [19–24] and this reduced number of hydrogen bonds leads to quite different structural and dynamical properties of liquid methanol compared to that of water.

Studies of vibrational spectral diffusion within the stretch band of normal or deuterated methanol by using ultrafast time resolved infrared spectroscopy provide a very powerful experimental means to investigate the hydrogen bond dynamics in liquid methanol at molecular level [25–28]. Vibrational frequencies of a hydrogen bonded molecule are known to be sensitive to its local solvent environment. When the surrounding environment fluctuates, the vibrational frequency also fluctuates. The time dependence of these vibrational frequency fluctuations is known as vibrational spectral diffusion. Recent experiments on vibrational spectral diffusion in liquid methanol involving time resolved pump–probe experiments have shown the presence of two time scales: A short time scale around ~0.1 ps and a long time scale of 1.6 ± 0.3 ps [25].

Many simulations using classical molecular dynamics with empirical force fields have also been carried out to study the dynamics of liquid methanol [15,16,22,23]. More recently, the technique of ab initio molecular dynamics [29,30] has also been employed to study liquid methanol which goes beyond the use of any empirical interaction potentials. However, the existing ab initio simulation studies have primarily focused on the structure, single-particle dynamics such as diffusion and orientational relaxation and pair dynamics such as relaxation of hydrogen bonds [31–37]. To the best of our knowledge, the dynamics of vibrational spectral diffusion in liquid methanol has not yet been studied through first principles simulations.

The present work deals with a first principles theoretical study of the vibrational spectral diffusion and hydrogen bond dynamics in liquid methanol. We have employed the method of ab initio molecular dynamics [29,30] for the generation of the trajectories and wavelet analysis [38–41] method for the time dependent frequency calculations along the trajectories. First, we analyze the equilibrium aspects of frequency-structure correlations in methanol. Mainly, the relations between the fluctuating stretch frequencies of OD bonds of deuterated methanol and associated D–O hydrogen bonds are found out. Subsequently, the dynamics of vibrational spectral diffusion are studied by means of frequency time correlation and spectral hole dynamics [41,42] calculations. The results of the dynamics are analyzed in terms of the damped intermolecular vibrations of intact hydrogen-bonded methanol pairs and also the lifetimes of free and hydrogen bonded states of OD bonds. The quantitative details of the time constants of frequency correlations and spectral shifts are found to depend on the frequencies of the tagged OD bonds. The results are analyzed
in terms of the dynamics of hydrogen bonds of varying strengths and also of free non-hydrogen bonded OD groups. By using the population time correlation function formalism, a first principles calculation of the kinetics of local structural relaxation of hydrogen bonds is also presented and the relations of such local structural relaxation with the observed dynamics of spectral diffusion are also discussed.

The rest of the paper is organized as follows. Section 2 contains the details of \textit{ab initio} molecular dynamics simulations and time series analysis for frequency calculations. In Section 3, the results of the frequency-structure correlations are discussed. Section 4 contains results of the vibrational spectral diffusion and hydrogen bond dynamics in liquid methanol. Finally, our conclusions are briefly summarized in Section 5.

2. \textit{Ab initio} molecular dynamics simulations

The \textit{ab initio} molecular dynamics simulations have been performed by using the Car–Parrinello method [29] and the CPMD code [43]. Our simulation system contains 32 methanol molecules in a cubic box of length 12.9\,Å. The size of the box corresponds to the experimental density of the methanol at 300 K [44]. The simulation box was replicated periodically in three dimensions and the electronic structure of the extended system was calculated by using the Kohn–Sham formulation [45] of density functional theory within the plane wave basis. The Troullier–Martins pseudopotentials [46] were used to treat the core electrons and the plane wave expansion of the Kohn–Sham orbitals was truncated at 70 Ry. A fictitious mass of 800\,au was assigned to the electronic orbitals and the coupled equations of motion describing the system dynamics were integrated using a time step of 5\,au (0.125\,fs). All hydrogen atoms were assigned the mass of deuterium to reduce the influence of quantum effects on the dynamical properties. Our choice of CD3OD in place of CH3OH ensured that electronic adiabaticity and energy conservation were maintained throughout the simulations for the chosen values of the fictitious electronic mass parameter and time step. We used the BLYP functional [47] in our electronic structure calculations as was also done in earlier \textit{ab initio} simulations of liquid methanol [31–37]. The initial configurations were generated using classical molecular dynamics simulations. Subsequently, the system was equilibrated for 15 ps in canonical ensemble using \textit{ab initio} molecular dynamics [29,43] and then the simulations were continued for another 50 ps in microcanonical ensemble for calculations of various equilibrium and dynamical quantities.

The time-dependent frequencies of OD bonds were calculated through a time series analysis using the so-called wavelet method. In particular, we have followed the method described in Ref. [39]. The basic idea behind the wavelet analysis is to express a time-dependent function $f(t)$ in terms of basis functions which are constructed as translations and dilations of a mother wavelet $\psi$

$$\psi_{a,b}(t) = a^{-\frac{1}{2}}\psi\left(\frac{t-b}{a}\right). \tag{1}$$

where the mother wavelet should decay to zero rapidly as $t \to \pm \infty$. The coefficients of this expansion are given by the wavelet transform of the $f(t)$, which is given as

$$L_f(a,b) = a^{-\frac{1}{2}} \int_{-\infty}^{\infty} f(t) \psi\left(\frac{t-b}{a}\right) dt \tag{2}$$

for $a > 0$ and $b$ real. For the mother wavelet, we have used the Morlet–Grossman wavelet [48]

$$\psi(t) = \frac{1}{\sigma\sqrt{2\pi}} e^{2\pi i \omega_0 t} e^{-\frac{t^2}{2\sigma^2}}. \tag{3}$$

with $\omega = 1$ and $\sigma = 2$. The scale factor $(a)$ of Eq. (2) is inversely proportional to the frequency, and thus the wavelet transform of Eq. (2) at each $b$ gives the frequency content of $f(t)$ over a time window about $b$. In the present work, we are interested in the OD stretch frequencies of deuterated methanol molecules. For this purpose, the time dependent function $f(t)$ for a given OD bond is constructed to be a complex function with its real and imaginary parts equal to the instantaneous OD distance and the corresponding momentum along the OD bond [41,49]. Subsequently, for a given time $t = b$, we determined the scale $a$ that maximizes the modulus of the corresponding wavelet transform as given by Eq. (2) and the frequency was determined from the optimized scale found at that point of time. The process was then repeated for all the OD bonds over the entire trajectory that was produced in the present simulations. We note that the Morlet-Grossman wavelet of Eq. (3) with the above mentioned values of the parameters $\omega$ and $\sigma$ was successfully used as the mother wavelet in many earlier studies of time series analysis of fluctuating frequencies from dynamical trajectories [39–41,49–52]. Some of these earlier studies also included calculations of stretch frequencies of OD and OH modes of aqueous systems [41,49–52]. In view of these earlier work, we preferred to use the same mother wavelet without any alteration of the parameter values.

3. Frequency structure correlations

The OD stretch frequency in a hydrogen bonded liquid is strongly correlated with the length of the hydrogen bond between the D atom of the OD group and the nearest oxygen atom of another molecule. In Fig. 1(a), we have shown the variation of the stretch frequency with time for one such OD mode in the system. In Fig. 1(b), the variation of the D–O hydrogen bond distance is also shown with time for the same chosen OD mode. A correlation between the two fluctuating quantities is evident. When the D–O distance is large, the frequency of the OD covalent bond in that particular time region also increases from its average value. We note that when the D–O distance decreases, the OD bond becomes more like that of a free methanol and, hence, its stretch frequency increases. On the other hand, when the D–O distance decreases, i.e. the hydrogen bond gets stronger, it is seen that the OD stretch frequency decreases from its average value. In Fig. 1(c), we have shown the fluctuations of the OD covalent bond distance for the

![Fig. 1.](image-url)
same bond and over the same time interval. We note that the length of the OD covalent bond fluctuates over a smaller distance with maximum amplitude found to be only about 0.25 Å above and below the average bond length of about 1 Å. The D·O hydrogen bond distance, on the other hand, could fluctuate over a larger distance, sometimes more than 1 Å from its average distance of about 1.8 Å as can be seen from Fig. 1(b). Of course, in some of these configurations of large D·O distance, the hydrogen bond is actually broken and R_{D-O} in that case merely means the distance between the deuterium of OD bond and its nearest oxygen of a neighboring methanol molecule. In view of this, the correlation of the fluctuations of stretch frequency of the OD bond with its bond length is not as clearly visible as it was for the hydrogen bond distance. Nevertheless, some correlations can still be extracted from Fig. 1(c). For example, the frequency fluctuations in the regions around 12.2 and 19 ps reveal an enhanced frequency associated with relatively shorter length of the OD covalent bond.

The relation between the frequency of OD bonds and the length of D·O hydrogen bonds, averaged over all molecules, is shown in Fig. 2(a). In this figure, we have shown the distribution of D·O hydrogen bond distance for three different values of the OD frequency within ±5 cm⁻¹. It is seen that as the frequency increases, the maximum of the corresponding distribution of D·O distance also gets shifted towards higher distance. On the other hand, the peak of the distribution of D·O distance is found to shift to shorter distance when the frequency is decreased. Similar results were found earlier for OD bonds in D₂O and HOD systems [41,42,49,53]. Due to the significant dispersion and overlap of the distributions, one can not assign a single frequency for a given D·O hydrogen bond distance. The above findings are more clearly revealed in Fig. 2(b) where we have presented contour plots of the conditional probability of finding a particular frequency for a given D·O distance. Clearly, one can not assign a single instantaneous frequency to a given D·O hydrogen bond due to substantial dispersion in the probability distribution. However, on average, the frequency of an OD bond is found to increase with increase of the length of the associated D·O hydrogen bond. Thus, a frequency-structure correlation is seen to exist on average where the frequency of an OD bond decreases or increases with the decrease or increase of the associated D·O hydrogen bond distance.

We also note that our calculated average stretch frequency is found to be 2225 cm⁻¹ which is somewhat red shifted from the average frequency of the corresponding experimental spectrum [25]. This discrepancy is likely due to the systematic errors introduced by the density functional, electronic fictitious mass, and finite basis set cutoff that are used in the electronic structure calculations and it may also depend on the size of the simulation system. Similar discrepancies were also found in earlier simulation studies of liquid D₂O systems for similar levels of calculations [41,49]. We note that a proper choice of the electronic fictitious mass is an important issue in carrying our Car–Parrinello simulations. This parameter introduces an extra inertia into the system, hence can affect its dynamics. Besides, a proper choice of this parameter is also required to ensure electronic adiabaticity during the simulations. While the value of 800 au for the fictitious mass parameter has been found to be acceptable for maintaining electronic adiabaticity for deuterated systems such as CD₃OD and D₂O [33,41,49], it may still introduce a systematic error in the vibrational frequency because of additional inertia effects. A detailed analysis of the extent of such systematic errors in vibrational frequencies due to the fictitious electronic mass is available in Ref. [54]. Regarding the effects of finite basis sets on the calculated vibrational frequencies, we note the work of Ref. [55] which shows that a converged basis set decreases the red shift in the OD stretching band of the IR spectrum. The systematic errors in the calculated frequencies could have been corrected by using a scaling factor as was done in many previous studies of aqueous systems. In the present work, we primarily focus on the dynamics of spectral diffusion and the normalized dynamics of spectral diffusion remains unaltered by use of any such scaling factors. Hence, we preferred to deal with the calculated frequencies as they were obtained from simulations and time series analysis without using any scaling factors.

4. Spectral diffusion and hydrogen bond dynamics

4.1. Frequency-time correlation function

The central dynamical quantity in the study of vibrational spectral diffusion is the frequency time correlation function which is defined as
\[ C_{\omega}(t) = \langle \delta \omega(t) \delta \omega(0) \rangle / \langle \delta \omega(0) \rangle^2 \]  
(4)
where \( \Delta \omega(t) \) stands for the fluctuation from the average frequency of an OD bond at time \( t \). The average is taken over the initial time and over all the OD groups present in the system. The decay of the correlation function is shown in Fig. 3 where a short time dynamics at around 100 fs followed by a slower decay extending up to a few ps is observed. Following earlier work [41,42], we fit the results to the following function
\[ f(t) = a_0 \cos \omega_0 t e^{-t / \tau_0} + a_1 e^{-t / \tau_1} + (1 - a_0 - a_1) e^{-t / \tau_2}, \]  
(5)
where the first term of the above function takes care of the slight oscillation that is found at around 200 fs. The values of the various terms of the above function are found to be as follows: \( \omega_0 = 98.2 \text{ cm}^{-1}, \tau_0 \sim 120 \text{ fs} \) and \( \tau_2 \sim 3.2 \text{ ps} \). These values are also included in Table 1. The oscillation at the short time is likely due to the underdamped motion of intact hydrogen bonded pairs of methanol molecules. To understand this aspect in more details, we also calculated the power spectrum of the relative velocities of oxygen atoms of initially hydrogen bonded methanol pairs (figure not shown here). Enhanced intensities in the region below
Following previous work \[57\], we write a simple kinetic equation

corresponding to the frequency time correlation, we have looked at the
dynamics of pump–probe signals of time dependent infrared
spectroscopic experiments on vibrational spectral diffusion. It is
assumed that at time \( t = 0 \), a laser pump pulse having a Gaussian
frequency profile burns a hole in the ground state having frequency
distribution of the form \[41,42\]

\[ P_h(\omega, 0) = P_{eq}(\omega)e^{-\frac{\omega^2 - \omega_0^2}{2\delta^2}}, \]  

(7)

where \( \omega_0 \) stands for the pulse center frequency and \( P_{eq}(\omega) \) denotes
the equilibrium distribution of all the OD frequencies present in the
system. Clearly, the initial distribution of the remaining frequencies
in the ground state is equal to \( P_{eq}(\omega) - P_h(\omega, 0) \). For the given sys-
tem, we have calculated time evolution of nonequilibrium distributions
of the remaining modes \( P_h(\omega, t) \) and also of the hole modes
\( P_h(\omega, t) \) after the hole is created at \( t = 0 \). The average frequencies

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Excitation</th>
<th>( \tau_0 )</th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \omega_x )</th>
<th>( \sigma_0 )</th>
<th>( \sigma_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{32}(t) )</td>
<td>–</td>
<td>0.12</td>
<td>0.12</td>
<td>3.1</td>
<td>98.2</td>
<td>0.23</td>
<td>0.41</td>
</tr>
<tr>
<td>( \Delta \omega_0(t) )</td>
<td>Blue</td>
<td>0.14</td>
<td>0.09</td>
<td>3.0</td>
<td>103.6</td>
<td>0.12</td>
<td>0.52</td>
</tr>
<tr>
<td>( \Delta \omega_0(t) )</td>
<td>Blue</td>
<td>0.16</td>
<td>0.12</td>
<td>6.0</td>
<td>103.7</td>
<td>0.22</td>
<td>0.58</td>
</tr>
<tr>
<td>( \Delta \omega_0(t) )</td>
<td>Red</td>
<td>0.14</td>
<td>0.12</td>
<td>5.9</td>
<td>116.3</td>
<td>0.22</td>
<td>0.42</td>
</tr>
<tr>
<td>( \Delta \omega_0(t) )</td>
<td>Red</td>
<td>0.14</td>
<td>0.10</td>
<td>3.4</td>
<td>109.8</td>
<td>0.10</td>
<td>0.40</td>
</tr>
</tbody>
</table>

150 cm\(^{-1}\) reveal the presence of intermolecular bending and
stretching vibrations of such hydrogen bonded methanol pairs.
Thus, the damped oscillations of the first term of Eq. (5) likely arise
from the fast intermolecular vibrations of intact hydrogen bonded
pairs of methanol molecules. The associated time constants of the
short time relaxation (\( \tau_0 \) and \( \tau_1 \) of Table 1) likely correspond to
the dynamic modulation of OD frequencies due to fast changes in
the characteristics of intact hydrogen bonds such as changes in the
hydrogen bond length and angle that can alter the OD frequencies.
Also, in order to investigate the origin of the slower relaxation
component of the frequency time correlation, we have looked at the
dynamics of hydrogen bonds by using the so-called population cor-
relation function method \[41,49,56–64\]. We calculate two hydro-
gen bond correlation functions \( S_{HB}(t) \) and \( C_{HB}(t) \) where \( S_{HB}(t) \)
describes the probability that an initially hydrogen bonded metha-
ol–methanol pair remains continuously hydrogen bonded at all
times up to time \( t \) and \( C_{HB}(t) \) describes the probability that a meth-
anol–methanol pair is hydrogen bonded at time \( t \) given that it was
also hydrogen bonded at time \( t = 0 \), independent of any possible
breaking in the interim time. The time integral of \( S_{HB}(t) \) can be
interpreted as the average lifetime of hydrogen bonds and it will
be denoted as \( \tau_{HB} \). The time dependence of the intermittent proba-
bility describes the local structural relaxation of hydrogen bonds.
After a hydrogen bond is broken, the pair of molecules can remain
as nearest neighbors for some time before they either reform the
hydrogen bond or diffuse away from each other. We define \( N_{HB}(t) \)
as the time dependent probability that a hydrogen bond is broken at
time \( t = 0 \) but the two molecules remain in the vicinity of each
other as nearest neighbors but are not hydrogen bonded at time \( t \).
Following previous work \[57\], we write a simple kinetic equation
for the decay of \( C_{HB}(t) \) as given below

\[ -\frac{dC_{HB}(t)}{dt} = k_{HB}C_{HB}(t) - k'_{HB}N_{HB}(t) \]  

(6)

where \( k_{HB} \) and \( k'_{HB} \) are the forward and backward rate constants,
respectively. The inverse of the \( k_{HB} \) can be interpreted as the
average lifetime of hydrogen bonds. The hydrogen bond between
the D and O atoms of two methanol molecules are based on the geo-
metric criteria that the D–O distance should be less than 2.45 Å
and O–O distance should also be less than 3.4 Å. These distance
cut-offs correspond to the first minimum of the intermolecular
D–O and O–O radial distribution functions (results now shown
here). The results of the continuous and intermittent hydrogen bond
correlation functions are shown in Fig. 4. On integrating \( S_{HB}(t) \), the
value of \( \tau_{HB} \) is found to be 2.8 ps. We have applied the
least square fit of Eq. (6) to the simulation results of \( C_{HB}(t) \) and
\( N_{HB}(t) \) in the region of \( 0 < t < 4 \) ps to obtain the corresponding rate
constants of hydrogen bond structural relaxation from the route of
intermittent correlations. The inverse of the forward rate constant
is found to be 3.0 ps which compares well with the lifetime as ob-
tained from the integration of the continuous correlation function.
Thus, the long time relaxation of vibrational spectral diffusion of
OD modes of methanol can be attributed to the breaking dynamics
of methanol-methanol hydrogen bonds. We note in this context
that the experimental value for this long-time relaxation of spectral
diffusion was found to be 1.6 ± 0.3 ps \[25\]. The discrepancy is likely
due to the use of BLYP density functional in the present calculations
which is known to provide a somewhat slower dynamics for rota-
tional and translational motion in dense hydrogen bonded systems.

4.2. Hole dynamics at different frequencies

We present calculations of the dynamics of a hole that is created
by the removal of a bunch of OD modes in different regions of the
inhomogeneous frequency distribution. The time evolution of such
initially created non-equilibrium distribution is closely related to
the dynamics of pump–probe signals of time dependent infrared
spectroscopic experiments on vibrational spectral diffusion. It is
assumed that at time \( t = 0 \), a laser pump pulse having a Gaussian
frequency profile burns a hole in the ground state having frequency
distribution of the form \[41,42\]

\[ P_h(\omega, 0) = P_{eq}(\omega)e^{-\frac{\omega^2 - \omega_0^2}{2\delta^2}}, \]  

(7)

where \( \omega_0 \) stands for the pulse center frequency and \( P_{eq}(\omega) \) denotes
the equilibrium distribution of all the OD frequencies present in the
system. Clearly, the initial distribution of the remaining frequencies
in the ground state is equal to \( P_{eq}(\omega) - P_h(\omega, 0) \). For the given sys-
tem, we have calculated time evolution of nonequilibrium distributions
of the remaining modes \( P_h(\omega, t) \) and also of the hole modes
\( P_h(\omega, t) \) after the hole is created at \( t = 0 \). The average frequencies
of the remaining and hole modes are then calculated from the following relations

\[
\frac{1}{N_i} \int d\omega P_i(\omega, t) = 1 - \frac{1}{N_i} \int d\omega P_0(\omega, 0).
\]

where \( i = r \) and \( i = h \) for the remaining and hole modes, respectively, and \( N_i = \int d\omega P_i(\omega, 0) \). To study the dynamics, we have created the hole in two different frequency regions: One centered at the red side at \( \omega_0 = \bar{\omega} - 100 \text{ cm}^{-1} \) and the other one centered at the blue side at \( \omega_0 = \bar{\omega} + 100 \text{ cm}^{-1} \) where \( \bar{\omega} \) is the average frequency of all the OD modes present in the methanol system. Following earlier work [41, 49], we employed a Metropolis Monte Carlo-like algorithm to create the hole of chosen distribution in the red or blue regions, and at different initial times so as to satisfy the distribution of Eq. (7).

Fig. 5. The time variation of the distribution of (a) hole and (b) remaining modes after hole creation in the blue side at time \( t = 0 \). The solid, dashed and dashed-dotted curves are for times \( t = 10 \text{ fs}, 50 \text{ fs} \) and \( 1.25 \text{ ps} \).

Fig. 6. The time variation of the distribution of (a) hole and (b) remaining modes after hole creation in the red side at time \( t = 0 \). The solid, dashed and dashed-dotted curves are for times \( t = 10 \text{ fs}, 50 \text{ fs} \) and \( 1.25 \text{ ps} \).

We have calculated the average frequencies of the hole and remaining modes from the time dependent distributions of Fig. 6 by using Eq. (8) and the results are shown in Figs. 7 and 8. It is seen that the overall decay pattern of the average frequencies is similar to that of the frequency time correlation function shown in Fig. 3. There is a fast decay at short times followed by an oscillation and a slower decay that extends up to few ps. It is found that the oscillation is more pronounced for the lower frequency modes, such as the remaining modes for blue and hole modes for red excitations. Due to involvement of the strongly hydrogen bonded OD modes of methanol molecules in the lower frequency region, the oscillation in the time evolution comes from the under-damped intermolecular vibrations of strongly hydrogen-bonded pairs of methanol molecules. It may be noted that both the modes i.e. bending and stretching modes of intermolecular vibrations can modulate the methanol OD frequencies, hence they can contribute to the short time oscillation of the hole dynamics. Values of 100–150 fs and 3–6 ps are found for the fast and slow time scales by fitting the

Fig. 7. The time variation of the (a) average frequency shifts of the hole modes after creation of the hole in the blue and in the red regions of the average frequency. The corresponding results after normalization by the initial frequency shifts are shown in (b). In both the figures, the solid and dashed curves correspond to hole creation in the blue and red regions, respectively. The grey solid curves in (b) represent the fits by a function of Eq. (5). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
calculated dynamics to Eq. (5) (Table 1). We note that the longer time constant corresponds to the lifetime of methanol-methanol hydrogen bonds. It may be noted that the relaxation has longer time constant for the lower frequency modes whereas a relatively faster relaxation is found for the higher frequency modes because the higher frequency modes are attached to weaker hydrogen bonds which have shorter lifetimes.

5. Summary and conclusion

In this work, a first principles theoretical study has been presented for the vibrational frequency-structure correlations and dynamics of spectral diffusion in liquid methanol without using any predefined empirical model potential. A time series analysis of the \textit{ab initio} simulation trajectory by using the wavelet method has been performed to calculate the frequency fluctuations. Our calculations reveal that although a one-to-one relation does not exist between the instantaneous frequency of the OD bond of a methanol molecule and the D-H hydrogen bond distance, such a correlation does exist on average. It is found that the frequency stretch frequency distribution and the results are analyzed in terms of the dynamics of intact hydrogen bonds and also of hydrogen bond breaking. The theoretical results are found to be in reasonably good agreement with the findings of recent spectroscopic experiments [25].

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References
