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The influence of chain dynamics on the

far-infrared spectrum of liquid methanol^{*}

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Abstract

Far-infrared absorption spectroscopy is used to investigate the low frequency (• 100 cm⁻¹) intermolecular interactions in liquid methanol. Using an intense source of far-infrared radiation, modes are elucidated at approximately 30 cm⁻¹ and 70 cm⁻¹ in the absorption spectrum. These modes are believed to arise from intermolecular bending and librational motions respectively and are successfully reproduced in an *ab initio* molecular dynamics simulation of methanol.

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I. INTRODUCTION

Liquid methanol is structurally very similar to liquid water. Both liquids form molecular associations through hydrogen-bonding networks; but methanol possesses only one donor hydrogen and a large methyl group that restricts the types of conformational structures that it can form with neighboring molecules. Both experimental and theoretical data suggest that at room temperature, the dominant structure in liquid methanol is a series of nonlinear hydrogen-bonded open chains^{1,2,3} rather than a topologically complex three-dimensional hydrogen-bonded arrangement, as is believed to exist normally in liquid water; conceivably, making methanol a somewhat easier associating liquid to study.

The local structure in liquid methanol plays an important role in the low frequency dynamics probed by methods such as far-infrared (FIR) spectroscopy. The hydrogen bond network in liquid methanol is conducive for forming strong intermolecular interactions that are sometimes visible in the IR absorption spectrum and the asymmetry of the methanol molecule leads to a complex dielectric relaxation spectrum that can also be investigated in an analysis of the frequency dependent complex permittivity. Both permanent and induced dipole moments contribute significantly to the low frequency FIR spectrum. Although the permanent dipoles are only dependent on molecular charge distribution, the interaction induced dipole moments depend on both the orientation and distance between molecules.⁴ Therefore, the presence of induced dipole moments introduces an intermolecular translational component to the dielectric relaxation spectrum. These motions, consisting of both rotational and translational elements, are not well separated in frequency and often appear in the same region of the infrared spectrum. In this study we will focus on the intermediate region of the total dipole density relaxation timescale (0.5 - 10 ps) where correlations between single molecule (induced dipoles) and collective dipoles are prominent. This period is coincident with the low frequency FIR spectral region $(5 - 100 \text{ cm}^{-1})$ that is accessible in the experimental and simulation measurements that will be presented in this work. The overall objective is to provide further insight into the molecular motions and intermolecular correlations that may contribute to and affect dielectric relaxation in liquid methanol.

II. EXPERIMENTAL

A. Simulation parameters

Electronic structure calculations were performed using the Kohn-Sham formulation of the density functional theory (DFT). The gradient-corrected BLYP functional^{5,6} was used in the DFT MD simulation using the Car-Parinello method⁷ and the CPMD code. Semi-local norm-conserving Martins-Troullier pseudopotentials⁸ were used for the C, O, and H atoms to limit the number of electronic states to contain only the valence electrons. The cutoff radii for the atoms were 1.11, 1.23, and 0.50 a.u. for the O, C, and H atoms respectively. The fictitious mass associated with the plane wave cutoff was chosen as 900 a.u. and the electronic states were expanded in a plane wave basis with a cutoff of 70 Ry. The simulation containing the 32 methanol molecules was performed in a cubic box with an edge of 12.9 Å for a time period of 8 ps under ambient conditions and at experimental density. The time step used for the simulation was 0.145 fs, and the temperature during the simulation was held steady by using a Nosé-Hoover thermostat. The initial configuration for the system was taken from the output of a 1 ns MD simulation utilizing the empirical force field developed by Haugheney *et al.*⁹

The infrared absorption coefficient is calculated using the dipole correlation function from the simulation and the following equation:

$$\alpha(v) \cdot n(v) = \frac{4\pi v \tanh(\beta \hbar v/2)}{3\hbar c V} \times \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle, \tag{1}$$

where $\alpha(v)$ is the frequency dependent absorption coefficient, n(v) is the frequency dependent refractive index, $\beta=1/k_bT$ and k_b is Boltzmann's constant, V is the volume, T is the temperature, c is the speed of light in vacuum, and **M** is the total dipole moment obtained from the final 5 ps of the simulation.

B. Experimental techniques

The methanol used in the experiments was obtained from Sigma and used directly without further purification. The FIR absorption spectra were collected at the SUNSHINE facility^{10,11} at Stanford University in a manner described in detail in a previous publication.¹² The spectral range of the FIR is determined by the Fourier transform of the particle distribution of the electron beam pulse and extends from 5 cm⁻¹ – 120 cm⁻¹. With each micropulse containing an energy of about 100nJ, a dispersive, Fourier Transform technique is used to determine the refractive index and absorption coefficient of the methanol sample directly without the use of a Kramers-Kronig type analysis. In each scan, an average of 30 pulses is used for an individual data point in the interferogram and ten independent scans are averaged together for an absorption measurement.

III. RESULTS AND DISCUSSION A. Background

In a molecular dynamic (MD) simulation study focusing on the frequency dependent permittivity of liquid methanol,⁴ the transverse and longitudinal components of the total dipole density were analyzed separately with the goal of gaining greater insight into the wave vector-dependence of dielectric relaxation in liquid methanol. In an IR experiment, it is only possible to probe the total dipole spectrum, but such an analysis is particularly useful for uncovering the origin of the modes observed in the experimental spectrum and for developing a better understanding about the dynamics taking place in the liquid. The transverse component of the dipole density is more sensitive to slow, orientational motions and from the longitudinal dipole it is easier to access fast inertial or oscillatory motions.^{13,14} An analysis of the frequency dependence of both components offers insight into both the intramolecular and intermolecular motions that influence the dynamics occurring in the liquid. In the \cdot 200 cm⁻¹ low frequency region in the work of Skaf *et al.*,⁴ modes from the transverse permanent dipole density were identified at 60 cm⁻¹ and 150 cm⁻¹.

The velocity autocorrelation function (ACF) is directly related to the density of states in the system and can also be related to the experimental infrared absorption

spectrum. A plot of the velocity ACF and its spectrum in the $0 - 100 \text{ cm}^{-1}$ region from the first principles MD simulation carried out in this work is shown in Fig. 1. In the spectrum the main diffusive peak is centered close to 25 cm⁻¹, and a much smaller shoulder in the spectrum is found at about 70 cm⁻¹. A secondary shoulder (not shown) also appears in the velocity ACF spectrum close to 130 cm⁻¹.



Figure 1: The center of mass velocity autocorrelation function (inset) and the corresponding power spectrum of methanol at 298 K.

To develop a better understanding about the origin of these peaks and how they can be related to motions in the molecule, the velocity autocorrelation spectrum is separated into components corresponding to the principal inertial axes of the molecule (inset in Fig. 2). As one would expect, each component contains a large contribution from the main diffusional peak. The contribution from the smallest moment of inertia peaks at a slightly higher frequency than observed from the larger inertial axes. A peak at a similar frequency (~25 cm⁻¹) has also been reported in studies focusing on the center of mass velocity autocorrelation of oxygen atoms in liquid methanol and has been ascribed to a "rattling" in a cage motion of a methanol molecule within a shell of its nearest neighbors.¹⁵ A more recent analysis¹⁶ has suggested that it is also consistent with an intermolecular bending mode; similar to the one detected in hydrogen-bonding dynamics

studies of liquid water.^{17,18} Only the intermediate axis (y - axis) contributes significantly to the higher frequency diffusional peak at 70 cm⁻¹. In the molecular axis coordinate frame, the y-axis is nearly parallel to the hydroxyl hydrogen atom and is therefore most likely to be influenced by the intermolecular hydrogen bond.



Figure 2: The velocity autocorrelation spectrum of methanol divided into components relating to the molecular principal axes. Solid line: x-axis; dashed line: y-axis; and dotted line: z-axis.

As noted in the previous section, the coupling of rotational and translational motions is influenced by both the geometry of the molecule as well as by the directional hydrogen-bonding interactions in the liquid. Both characteristics have a strong influence on the intermolecular dynamics taking place in liquid methanol. Oriented in linear chains, the methanol molecule is able to freely rotate about the intermolecular hydrogen bond; therefore, most of the diffusion relaxation occurs in this manner.² Unlike water were librational motions are the dominant mechanism for promoting relaxation, most of the rotational diffusion motion in methanol is believed to take place about the methanol intermediate axis. With only one small inertial axis, intermolecular stretching motions between neighboring molecules in the methanol hydrogen-bonded chain network becomes the most efficient means for breaking hydrogen bonds in the liquid.¹⁹ With this in mind, it is possible to envision how a coupling between slow rotational motions and oscillatory motions in the liquid might occur. Returning to the • 100 cm⁻¹ FIR spectrum reported in the study of the wave vector-dependent dipole density,²⁰ peaks were identified at 55cm⁻¹ and 85cm⁻¹ in the transverse and longitudinal dipole spectrum respectively. Considering that the transverse and longitudinal parts of the dipole density accentuate different types of motions within the same mode, it seems relevant to point out that a peak at 55cm⁻¹ has also been identified in our simulation spectrum of liquid methanol and has been found to be strongly correlated with the orientational motion of the methyl group.

Earlier MD investigations^{2,21} focusing on the hydrogen-bonding correlations in liquid methanol have revealed that the hydrogen-bonding rearrangement process consists of both a slow and a fast process. The slow process occurs over a broad spectral range most accessible in microwave dielectric spectroscopy experiments. But the relaxation of the fast process is within the experimental spectral range investigated in this study and based on its characteristic time (~ 0.5 ps) possibly corresponds to the hydroxyl atom motion identified in the center of mass velocity ACF spectrum in Fig. 1. Further analysis of this very broad peak, centered about 70 cm⁻¹ in the velocity ACF spectrum, has suggested that this motion can be attributed to the torsion of the methanol hydroxyl hydrogen in the direction of the hydrogen bond.

B. Hydrogen-bonding

Results from earlier MD simulations have suggested that reorientation of permanent dipoles in the liquid is responsible for most of the infrared absorption in liquid methanol.^{22,4} But with growing evidence suggesting that intermolecular translational motions also play a crucial role in methanol relaxation processes,²³ it seems prudent to explore the role of hydrogen-bonding correlations in the liquid in further detail. It is likely that oscillations within the liquid methanol hydrogen-bonding network will lead to considerable modulation of the induced molecular dipole moments, and as a consequence may contribute rather significantly to the IR absorption spectrum. In the CPMD simulation results presented in this work, the intramolecular anharmonicity and polarization effects in the liquid are considered by default due to the Car-Parrinello method.⁷ Inclusion of polarization is not essential for an analysis of the intermolecular vibrational modes, but will become considerably more important later in a discussion regarding the total dipole spectrum. In Fig. 3 the 0 - 100 cm⁻¹ region of the hydrogenbonded pair correlation spectrum of the liquid methanol system is shown. In this analysis, a methanol molecule is considered to be hydrogen-bonded by using the following criteria:

- (1) The center of mass distance is less than 3.8 Å,
- (2) The r($O^{\bullet\bullet\bullet}H$) distance is smaller than 2.5 Å,
- (3) \angle HO•••O angle is smaller than 30°.

The values used correspond to the first minimum of the radial distribution function (RDF) of liquid methanol.⁹ Fluctuations within the hydrogen bonds are characterized by a correlation function,

$$c(t) = \frac{\left\langle h_b(0) \cdot h_b(t) \right\rangle}{\left\langle h_b^2 \right\rangle},\tag{2}$$

that is averaged over all pairs of hydrogen bonded molecules and has a value of either 0 or 1 based on the geometrical criteria used to define hydrogen-bonding associations. Motions within the hydrogen bond reference frame (top portion of Fig. 3) are divided with respect to those taking place along the hydrogen bond (A), orthogonal to the bond (B), and motions out of the methanol hydrogen bonding plane (C).



Figure 3: Hydrogen-bonding correlation function (inset) and spectrum of methanol at 298 K calculated using Eq. (2). Correlations in the spectrum are separated into parts that describe hydrogen-bonding associations defined by a hydrogen-bonding reference frame shown in the top portion of the figure and described in greater detail in section III.B. Dotted line: A-axis; solid line: B-axis; and dashed line: C-axis

Motions arising from translations perpendicular to the hydrogen bond (B-axis) are close in frequency to peaks observed in the velocity ACF spectrum. The similarity to the velocity ACF spectrum is not entirely unexpected in view of the fact that both correlations reflect the influence of nearest neighbor interactions with respect to the local dynamics. The connection with translational motions orthogonal to the hydrogen bond can also be explained in terms of the molecules tendency to diffuse in a direction where the hydrogen bond restoring force is not as strong. One distinct aspect of examining the nearest neighbor correlations with respect to the hydrogen-bonding frame is that contributions to the intermolecular dynamics from the methyl group motion become more apparent. The broad peak centered about 25 cm⁻¹ in Fig. 3 as well as in the in velocity ACF spectrum in Fig. 1 is consistent with the intermolecular bending mode previously reported in the work of Gaberoglio *et al.*^{16,24} Although the 25 cm⁻¹ peak spans nearly 40 cm⁻¹, a contribution from a much smaller band, resulting from motions out of the hydrogen-bonding plane (C-axis), can also be detected at about 32cm^{-1} . The effect of the methanol molecule asymmetry, in addition to the directional hydrogen bonds, again

appears to influence the orientational correlations taking place in the liquid. We find that the 32cm⁻¹ mode originates from torsional motion of the methyl hydrogen atoms, coupled to the intermolecular bending mode. In the solid state these motions would be well separated, but in a dense liquid system they occur on the same length and timescale.

Another occurrence of rotational – translational coupling within the hydrogenbonding framework is observed in the > 40 cm⁻¹ region of the spectrum. A smaller contribution to the spectrum resulting from translational motion perpendicular to the intermolecular hydrogen bond is found at approximately 80 cm⁻¹ in Fig. 3. This band is close in frequency to the one identified in the center of mass velocity ACF spectrum involving motion of the hydroxyl hydrogen atom (Fig. 1); it also appears at a similar frequency as the reported molecular reorientation about the intermolecular hydrogen bond identified in the angular velocity ACF spectrum of MD studies on liquid methanol.^{2,22} A band arising from a correlation (about the C-axis) involving yet another methyl group orientational motion also appears in the spectrum at approximately 55 cm⁻¹. Interestingly in Fig. 3, there is a noticeable absence of motion about the A-axis (along the hydrogen bond) in the < 100 cm⁻¹ region of the hydrogen-bonding spectrum. Bands arising from motion along the A-axis appear at approximately 130 cm⁻¹ and 150 cm⁻¹ (not shown) in the low frequency region (• 200 cm⁻¹) of the correlation spectrum.

There has already been some indication that there is a close association between short-range correlations and long range collective reorientational motions in the overall molecular relaxation process from MD wave vector-dependent analyses of dielectric relaxation in liquid methanol.^{4,25} But more recently, the influence of hydrogen bond dynamics on the relaxation process has also been explored in detail experimentally with IR pump-probe experiments measuring the decay of the hydroxyl stretch excitation of methanol in varying concentrations of carbon tetrachloride.^{26,23,27} The response following the excitation has been successfully modeled as a biexponential process with a fast and slow time scale. The fast decay (~1.7 ps) features a limited reorientational motion in which the hydroxyl atom fluctuates within in a restricted radius, presumably as a result of the hydrogen bond which limits its mobility; and in the longer decay time (~17 ps) full reorientational diffusion occurs.²⁶ From these experiments it was also determined that in concentrated solutions of methanol, the decay of the excited population of molecules takes place on a faster timescale. A similar phenomenon has also been reported in IR pump – probe experiments of liquid water.^{28,29,30} Further analysis of the experimental results uncovered that short range dipole-dipole correlations, facilitated by the hydrogen-bonding network, are responsible for transferring the excess excitation energy throughout the liquid system and as a consequence relaxation occurs more rapidly.

C. Relaxation pathway and low frequency modes

MD simulation studies on the three-dimensional local structure of methanol have revealed that hydrogen-bonded chains in the liquid prefer a local parallel arrangement similar to the arrangement found in the solid.¹ An experimental study on the collective contributions to dielectric relaxation of hydrogen-bonded liquids recently uncovered that cross correlations between parallel dipole correlations, such as those that exist in the liquid methanol chain network, lead to a slowing down of the relaxation process.³¹ A similar conclusion was reached after an analysis of cross correlations occurring

between permanent and induced dipole moments in the transverse and longitudinal components of the dipole density in liquid methanol.⁴ Results from this study revealed that cross correlations lead to an enhancement of long-range orientational correlations in the transverse component of the dipole density; which is consistent with the experimental observation of the collective contributions. In contrast, correlations between dipoles were found to reduce the orientational part of the longitudinal dipole density; making the longitudinal component more sensitive to short-range intermolecular fluctuations. Earlier theoretical work on dielectric relaxation highlighted the importance of translational modes in reducing orientational correlations in dipolar liquids; ultimately leading toward faster exponential or Debye –like decay.³² Incidentally, the mechanism for energy relaxation transfer detected in the anisotropy decay measurements of liquid methanol discussed in the previous section, is believed to occur through short-range interactions between dipoles oriented in different directions.³³ Insight into the short-range translational response after excitation has been gained from transient hole burning experiments of liquid methanol.²³ The spectral diffusion dynamics observed after excitation of the hydroxyl stretch was found to take place on two time scales. In this case, the fast response occurs within about 200 fs followed by a considerably slower diffusional process (~ 1.6 ps). During the slower translational process, relaxation is accompanied by a red shift in the hydroxyl stretch band. The red shift of the band has been attributed to short-range structural fluctuations between molecules that lead to the weakening of the hydrogen bond. Oscillations in the hydrogen bond network have also been identified in a theoretical analysis focusing on the collective longitudinal density in liquid methanol.¹⁹ In this analysis, a peak (~ 120 cm⁻¹) was identified in the calculation of the longitudinal density fluctuations; and it was ascribed to a cooperative motion of methanol molecules within the liquid hydrogenbonded chain network. Based on the similarity to modes in lattice dynamical calculations in a polycryastalline sample of methanol, it was speculated that the motions in the room temperature liquid are closely related to the dynamics in the crystal structure. Subsequent work investigating the collective hydrogen-bonding dynamics in methanol chains using an instantaneous normal mode (INM) analysis, focusing on the translational motions in the liquid also uncovered bands located between 120 - 130 cm⁻¹ that were assigned to collective "stretching" motions within methanol hydrogen-bonded chains.16,24

Further insight into the relaxation pathway of liquid methanol has also recently emerged from multidimensional spectroscopy methods. From 3-D spectroscopy experiments, an extensive study on the relaxation pathway in liquid methanol has revealed that excitation leads to the selective hydrogen bond breaking of molecules that possess stronger hydrogen bonds.²⁷ In liquid methanol this corresponds to molecules that have both donor and acceptor hydrogen bonds. Results from these experiments have suggested that the breaking of hydrogen bonds in this particular subset of molecules leads to the subsequent excitation of modes that are more efficient at returning the system to equilibrium. In particular, due to anharmonic coupling between modes, OH bending modes are the dominant motions excited directly following the excitation of methanol molecules with stronger hydrogen bonds. Perhaps this is not entirely unexpected considering the close connection between OH bending modes and the intermolecular hydrogen bond. It is also worth noting that in the sequence of events

leading toward energy dissipation along this route, energy transfer also leads to the excitation of methyl rocking modes. This seems particularly relevant considering that the dominant modes excited in the intramolecular transfer pathway essentially describe the motions that have been assigned to the methyl and hydroxyl group motions in the > 40 cm⁻¹ region of the hydrogen-bonding spectrum of methanol in Fig. 3 and the velocity ACF spectrum in Fig. 1 respectively.

Vibrational echo spectroscopy experiments have also been used to investigate the underlying mechanisms contributing to hydrogen bond dissociation and reformation in liquid methanol.^{34,30} Results from these experiments have revealed that the entire relaxation process occurs on three distinct time scales. On the shortest timescale, a portion of excited molecules undergoes direct hydrogen bond dissociation within ~200 fs. This direct route is most likely the result of vibrational relaxation as well as librational motions about the smallest moment of inertia, which would provide the most direct pathway toward hydrogen bond dissociation. Coincidently, Skaf et al.^{4,25} also observed that the early collective dipolar response to excitation in methanol and methanol-rich mixtures was attributed to librational motions about the methanol x –axis. An indirect approach leading toward the breaking of hydrogen bonds occurs within an intermediate timescale (~2 ps).³⁵ Through a sequence of intermolecular and intramolecular interactions (described in the previous sections), energy is transferred by a combination of long and short-range correlations that ultimately lead to hydrogen bond dissociation. Perhaps it is not entirely surprising that the intermediate timescale in the relaxation pathway overlaps with the restricted rotational motion detected experimentally in the anisotropy decay of liquid methanol as well as with the translational motions associated with spectral diffusion observed in the transient hole burning experiments discussed in section III.C.

In the final stage of the relaxation process excess energy in the system is fully dissipated with the reformation of hydrogen bonds. Results from IR pump -probe experiments have indicated that this process is distinct for molecules for which hydrogen bond dissociation has occurred directly and for molecules where hydrogen bonds have been broken by energy relaxation transfer.³⁵ Hydrogen bonds that are broken directly still possess excess energy after initial relaxation and as a consequence undergo further relaxation through structural reorganization before undergoing fast hydrogen bond reformation within 7 ps. The recovery rate of hydrogen bonds broken through the indirect pathway (20 ps) occurs on a time scale that is slightly longer than the reported full orientational relaxation time detected in the experimental rotational anisotropy decay of the excited OH stretch vibration. Taking into account the difference between the collective and molecular reorientational times, 1 and 2 respectively,^{36,37} the hydrogen bond reformation process also takes place after the long time exponential decay of the transverse component of the collective dipolar relaxation observed in MD simulations of liquid methanol⁴ as well as the slowest relaxation time measured in experimental terahertz and dielectric relaxation spectroscopy experiments.^{38,39} In all instances, the long time decay prior to the reported hydrogen bond reformation time is ascribed to diffusional-rotational relaxation. We find in this work that both the 55cm⁻¹ and 75 cm⁻¹ mode arise from librational motions about the methanol y –axis at intermediate times involving motion of the methyl and hydroxyl group respectively.

D. Experimental and simulation FIR spectra

Far infrared spectroscopy is also a useful probe for investigating the low frequency dynamics in liquid methanol. For a system with only permanent dipoles, the absorption spectrum describes collective reorientational motion. Additionally, for methanol, libration about the two largest moments of inertia (y and z–axis) also produces bands that are visible in the low frequency (• 200 cm⁻¹) IR spectrum. In a polarizable liquid system like methanol, it is possible that FIR absorption also reflects short-range interactions that would appear as induced dipole bands in the spectrum. The 0 - 100 cm⁻¹ region of the *ab initio* total dipole spectrum of liquid methanol is shown in Fig. 4 where a prominent peak is found at about 75 cm⁻¹. In the > 100 cm⁻¹ region of the spectrum (Fig. 5), there is a very broad band centered at about 140 cm⁻¹ and in the higher frequency intermolecular region (inset in Fig. 5) a large peak is centered at about 600 cm⁻¹. These peaks have also been identified in other experimental and simulation studies of liquid methanol and are believed to arise from librational motions.^{4,40,41}



Figure 4: $0 - 100 \text{ cm}^{-1}$ region of the computed IR absorption spectrum of methanol at 298 K using Eq. (1).

To clearly identify the types of motions that contribute to the peaks that are observed in the infrared spectrum, the total dipole simulation spectrum is divided into components that reflect the principal axes of the molecule. In Fig. 6 the x, y, and z components of the *ab intio* dipole spectrum in the 0 - 100 cm⁻¹ region are shown. This region will be the primary focus since it coincides with the region that we are capable of exploring experimentally. As expected, it is the intermediate axis (y-axis) that predominately contributes to the 75 cm⁻¹ mode in Fig. 6. There is also a noticeable

absorption band centered at about 35 cm^{-1} that was somewhat less apparent in Fig. 4. The 35 cm^{-1} band is dominated by motions involving the molecular x - axis.



Figure 5: Computed IR absorption spectrum of methanol in the $100 - 200 \text{ cm}^{-1}$ intermolecular region. In the inset the $250 - 800 \text{ cm}^{-1}$ spectral region is also shown.



Figure 6: The $0 - 100 \text{ cm}^{-1}$ region of the computed IR absorption spectrum separated into contributions relating to the molecular principal axes. The dashed-dot-dotted line indicates the x-axis, dashed line the y-axis, and the solid line the z-axis.

A peak at a similar frequency was also identified in the hydrogen-bonding correlation spectrum in Fig. 3 and was attributed to torsional motion of the methanol hydrogen atoms, coupled with the intermolecular bending mode. Ironically, the intermolecular bending mode is noticeably absent from the IR spectrum. The inactivity of translational modes in the IR spectrum has been addressed in a study of liquid methanol using a chemical potential equalization (CPE) method.⁴² Based on an analysis of induction effects in the liquid, it was determined that induced dipole moments are effectively canceled by cross correlations between induced and permanent dipoles; hence, the purely translational modes are not expected to be visible in the IR spectrum. It is also interesting to point out that although the 140 cm^{-1} mode is not displayed in Fig. 6; it also appears to be strongly influenced by methyl group motion. The low frequency side $(\sim 130 \text{ cm}^{-1})$ of the broad band is strongly influenced by the internal rotational of the methyl group while the higher frequency side ($\sim 150 \text{ cm}^{-1}$) can be attributed to librational motions about the principal axis. Earlier in this section, it was speculated that the correlated fluctuations in the hydrogen bond length reported in simulation studies of liquid methanol^{19,16,24} might be related to the diffusional dynamics detected in transient hole burning experiments.²³ The peaks identified as collective "stretching" modes between 120 - 130 cm⁻¹ in the INM study of the translational dynamics in liquid methanol^{16,24} extend over the same frequency region as the internal rotation of the methyl group (130 cm⁻¹) in the CPMD dipole spectrum and also appear close in frequency to the principal axis librational motion at 150cm⁻¹. Based on the proximity of the peaks, it is probable that the structural evolution of the hydrogen bond network in spectral diffusion may consist of a complicated mixture of short-range translational motions as well as rotational/librational motions.

In Fig. 7, the total dipole spectrum from the CPMD simulation is compared with the experimental FIR absorption spectrum in the same spectral region. Although there is a noticeable lack of intensity in the • 50 cm⁻¹ region of the CPMD spectrum in Fig. 7a, the computed and experimental spectrum do show some similarity. In Fig. 7b, the experimental FIR absorption spectrum features a weak shoulder at about 35 cm⁻¹, that is analogous to the peak observed in the x-component of the $< 100 \text{ cm}^{-1}$ region of the computed dipole spectrum in Fig. 6; and a prominent peak appears in the spectrum at about 70 cm⁻¹. Although the 35 cm⁻¹ mode appears at a similar frequency in both spectra (Fig. 7a and 7b), the 75 cm⁻¹ peak is somewhat blue-shifted in the CPMD spectrum when compared to the experimental spectrum. Due to the close association of the 75 cm⁻¹ mode with O-H bond dynamics, this might suggest that the hydrogen-bonding in the simulation system is stronger than the bonding in the experimental system. One curious feature missing from both spectra is the 55cm⁻¹ mode identified in the hydrogen-bonding analysis in section III.B. It is unclear if this band is simply IR inactive or if the contribution is too small to be resolved in the infrared spectrum. This is a topic that will be pursued further in a future publication.



Figure 7: The 10 - 100 cm⁻¹ region of the computed IR absorption spectrum of methanol at 298 K (solid line with open circles). Experimental IR absorption spectrum of methanol at 298 K (solid line with filled circles) at a 2 cm⁻¹ resolution

IV. CONCLUSIONS

We have used an intense source of FIR to investigate the low frequency dynamics in liquid methanol. To gain greater insight into the microscopic origin of the modes that appear as bands in the IR absorption spectrum, the total dipole spectrum from an *ab initio* MD simulation of the liquid has been calculated and the local hydrogen-bonding environment of methanol has been analyzed. We report bands in the • 100 cm⁻¹ region of the experimental spectrum of methanol that have been identified as intermolecular bending and librational modes.

The IR analysis of methanol has generally relied on the higher frequency librational region to interpret the dynamics occurring in the liquid. We believe that the present work will offer complimentary details about the low frequency intermolecular interactions in liquid methanol and additionally provide further confirmation about the presence of some modes that have previously only been explored in theoretical and simulation studies on methanol.

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