Effect of Pressure on Hydrogen Bonding in Liquid Methanol

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We have investigated the effect of pressure on the hydrogen bonding in liquid methanol using Raman spectroscopy. Specifically, we have measured the OH and CO stretching modes and assigned the bands, in agreement with recent IR and crossed molecular beam experiments on methanol clusters. At about 7 to 8 kbar, we note indications that the intrinsic nature of the methanol clusters in our samples has changed. Our results provide support for and extend conclusions derived from Monte Carlo simulations, explain anomalies observed by previous researchers, and provide new insights into general hydrogen-bonding phenomena.

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Methanol is the prototypical model for the study of general hydrogen-bonding phenomena, as it is the simplest system exhibiting both hydrogen bonding and nonpolar interactions, a combination of importance and strong relevance to biochemical systems. Despite its apparent simplicity, liquid methanol demonstrates complex and sometimes puzzling behavior that is not well understood, though hydrogen bonding evidently plays a key role. A clear understanding of the effect of pressure, temperature, or dilution on the hydrogen-bonding interactions needs to be developed, to provide important insight into the nature of this fundamental liquid system [1].

Bridgman argued [2] that increasing pressure on liquid water should lead to growing complexity of the "molecules" (i.e., clusters). NMR measurements of the monomer-tetramer equilibrium in methanol mixtures [1] indicate that pressure promotes the formation of hydrogen bonding, although it is noted that the situation could be different for the neat liquid. Similarly, molecular dynamics simulations [3] suggest that hydrogen bonding increases with rising pressure in glycerol. In contrast, Monte Carlo (MC) simulations [4] indicate that hydrogen bonding remains almost unchanged up to 15 kbar in liquid methanol.

Raman spectroscopy has been shown to be a powerful tool to understanding hydrogen-bonding phenomena in liquid water [5–8], though unfortunately to a lesser degree for related systems. Mammone *et al.* [9] have pointed out that the OH stretching bands in liquid methanol are very weak, broad, and difficult to resolve in the Raman spectra at high pressure, especially since the OH bands are severely overshadowed by the nearby CH stretching modes.

A recurrent discussion in the literature refers to the relative strengthening of hydrogen bonding with pressure [9,10], since the experimental redshift of the OH vibrations with increasing pressure in alcohols has been interpreted as a weakening of the OH mode induced by the strengthening hydrogen bonding. Monte Carlo simulations question this interpretation [4], however. Further complicating matters, Raman measurements of a 4:1 methanol-ethanol mixture demonstrate an unusual minimum in the methanol CO stretching frequency with pressure that has been interpreted as reflecting peculiar strengthening-softening behavior of hydrogen bonding as a function of pressure [10]. A high-pressure study of ethanol [11] exhibits similar atypical behavior, though to a lesser extent. Unfortunately, both studies fail to study the pressure dependence of the liquid state OH stretching bands in the relevant pressure regime.

In this Letter, we report Raman spectra of the OH and CO bands in liquid methanol (Aldrich spectroscopic grade). We utilized a sapphire anvil cell [12] to pressurize samples, as sapphire has the advantage of a fluorescence-free spectral window up to 3800 cm^{-1}. Raman signals were obtained using the 488.0 nm line of an Ar^{+} laser and collected in backscattering geometry using an ISA HR460 spectrograph coupled to a CCD multichannel detector. Owing to the weakness of the OH stretching bands, collection times of up to 20–30 min were needed. Slit widths providing resolutions of 4 and 1 cm^{-1} were used to record the OH and CO spectral regions, respectively. Pressures were determined within 1 kbar by measuring the Raman phonon of diamond chips interspersed throughout the sample [12].

In Fig. 1(a), we plot the broad OH stretching band at selected pressures. We note the apparent redshift and broadening of the band profile with increasing pressure. Since little is known about the nature of this complex band, its interpretation is controversial and depends critically on the microscopic model proposed for the liquid. A proposed interpretation of the OH stretching region of liquid methanol [13] is based on the bifurcated-hydrogen-bond model [14]. The OH band was adequately fit by at least three Gaussians, as confirmed with overtone measurements [15], that were ascribed to clusters containing linear, bifurcated, and trifurcated hydrogen bonds [13].

Since such assignments are yet to be reconciled with previous observations [16–20], we favor those indicated by crossed molecular beam experiments [17–20]. These

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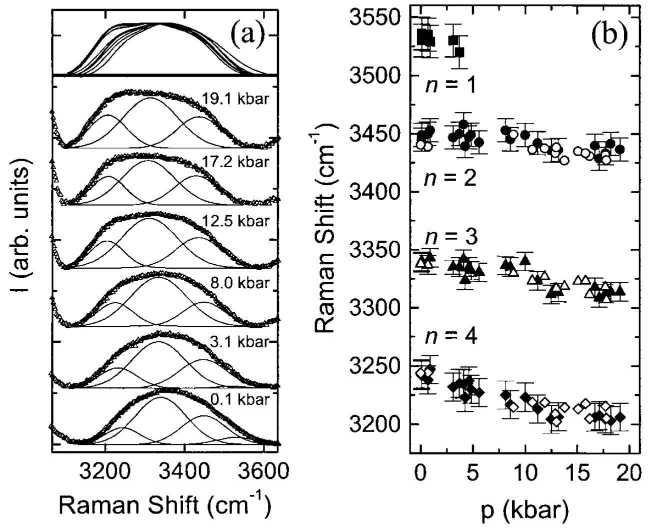

FIG. 1. (a) Pressure dependence of the OH stretching band profile in liquid methanol. A three-Gaussian summation was used to fit the spectra over the whole range of pressures. The experimental spectra are scaled for comparison. The resulting spectra are grouped together on the top, showing a characteristic isosbestic point at about 3330 cm^{-1}, which is indicative of a chemical equilibrium between different species [5]. (b) Frequencies of the three/four Gaussian used to fit the OH stretching profile as functions of pressure (see text). Open and closed symbols stand for different experimental runs.

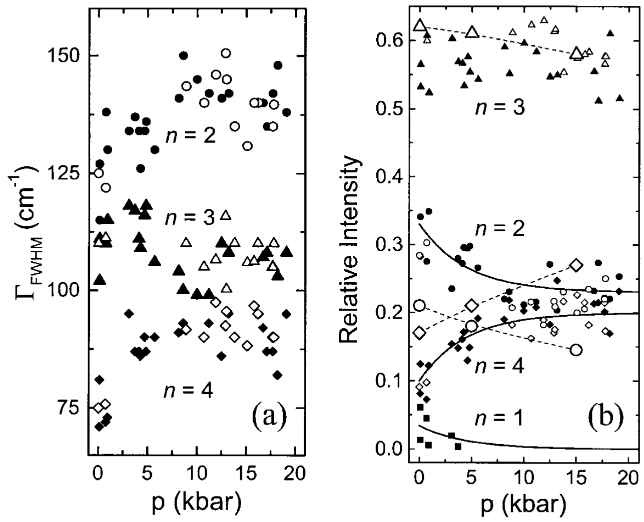

FIG. 2. Widths (FWHM) (a) and relative intensities (b) of the Gaussian fits to the OH stretching profile as functions of pressure. Relative intensities are calculated as the ratio between the area of a given band and the total area. Symbols as in Fig. 1. Large open symbols and dashed lines represent MC results from Ref. [4]. All lines are guides to the eye.

latter investigations confirm that the OH stretch of monomer methanol appears at about 3680 cm^{-1}. Higher order clusters appear to be sequentially shifted to lower energies. Methanol dimers give rise to a complex band between 3480 and 3520 cm^{-1} [21]. Trimer complexes exhibit a broad structure between 3370 and 3460 cm^{-1}, and tetramer and higher aggregates demonstrate broad features between 3200 and 3300 cm^{-1}. Recent results on methanol trapped in nitrogen and argon matrices [16] are consistent with these values. Similarly, *ab initio* [22,23] and optimized intermolecular potential calculations [24] also confirm these values for small clusters in the gas phase.

Within the context of this latter discussion, the main contributions to the complex OH stretching spectra observed in liquid methanol plausibly originate from molecular entities similar to these clusters. The results of our Gaussian analysis are summarized in Figs. 1 and 2. All of our spectra are explained as the sum three or four Gaussians with pressure-dependent intensities [Fig. 1(a)]. Our atmospheric pressure frequencies, 3456(12), 3340(5), and 3247(8) cm^{-1}, are in excellent agreement with determinations by Ref. [13] interpolated to room temperature.

We observe a slight variation of the FWHM [Fig. 2(a)] at low pressures, indicating a continuous evolution in the molecular environment of each cluster. For pressures above 7–8 kbar, the FWHMs remain constant to within 10 cm^{-1}. Taking into account that in the liquid state the bands will widen and shift to lower frequencies due to increased intermolecular interactions, our frequency distribution is in agreement with previous studies [16–20,23]. In spite of the uncertainties introduced by band broadening that are already evident in the gaseous state, it is reasonable to assume that the pressure variation of the integrated intensities reflects a change in the concentrations of the aggregates in the liquid. Finally, although higher order aggregates are believed to exist in the liquid, the main contribution to the lowest frequency band even at modest pressures are observed to arise primarily from tetramers owing to their high stability [1,23]. For pressures below 4 kbar, we find enhanced fits to our data if we assume that a small amount of monomers exist. An estimate of monomer concentration based on our four Gaussian fits yields values in agreement with MC simulations [4].

From Fig. 1(b), we note that frequencies remain approximately constant at low pressure, while Fig. 2(b) shows that the relative intensities change smoothly. This result argues that pressure favors the formation of higher order clusters [2,25]. However, at higher pressures, both relative intensities and FWHM remain constant, while frequencies are slightly but steadily lowered with basically the same slope. Thus, we argue that pressure no longer leads to increasing complexity of the methanol clusters but to a simple compression process of the liquid that induces a cooperative decrease in the frequency of the OH bands and an increase of the CO stretching bands (see below). This behavior is interpreted as a strengthening of hydrogen bonding with pressure [3,4], which is already observed in going from the gas to the liquid phase. Our results thus support the interpretation that increasing pressures shift the cluster concentration equilibrium towards higher orders until about 7 to 8 kbar. Above this pressure, the concentration equilibrium appears unaltered, though the hydrogen-bonding interactions appear to strengthen.

Our current interpretation supports and extends the conclusions derived from previous MC simulations [4]. A direct comparison between MC results and our present data can be established if one considers that n-mers clusters resemble groups of n-oxygen atoms that contribute significantly to the first peaks of the O-O radial distribution function in the liquid. Within that approximation, a detailed description of the cluster geometry is not needed, since various molecular arrangements can correspond to the same structure factors, as concluded in a recent reverse Monte Carlo study [26]. A comparison of the relative concentration of methanol clusters with the oxygen neighbor distribution obtained in Ref. [4] is included in Fig. 2(b). The MC calculations are in remarkable agreement with our results. Unfortunately, the simulations were carried out at only three pressures, precluding the observation of the constancy of the cluster concentration at high pressures.

We can extend our interpretation of the OH vibrations to encompass other modes in the liquid methanol spectrum, namely, that other modes consist of a fixed number of bands that vary position, intensity, and FWHM as a function of pressure (or temperature) in a similar way as the OH profile does. A notable exception is the CH stretching region, since Fermi resonance occurs between the CH symmetric stretch fundamental and a CH bend overtone [27]. However, Fermi coupling is unlikely in the OH stretching region, as the length of the hydrogen bond in liquid methanol is about 2.8 Å [28]. In addition, although formation of a CH$\cdots$O hydrogen bond has been recently suggested [29], its strength is an order of magnitude smaller than the strength of the OH$\cdots$O bond.

We now attempt to cast light on the enigmatic minimum observed in the CO stretching band with increasing pressure [10] that is not observed in the other modes. Crossed molecular experiments [17] indicate that dimers give rise to two well separated bands, while trimers and larger aggregates yield wide bands centered between those from the dimer.

Neglecting noncoincidence effects [30], we modeled the complex CO stretching Raman spectra of liquid methanol at room conditions with four bands [Fig. 3(a)], by fixing their relative areas to reflect the relative composition obtained from our OH band results. In Table I, we compare crossed molecular beam experiments with ours at low pressure. The agreement is extraordinarily good, taking into account the expected shifts in the liquid phase (about 9 cm^{-1} for all the bands).

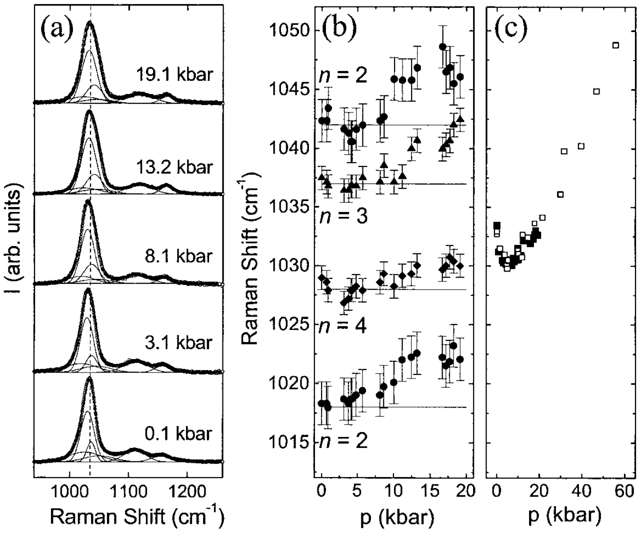

FIG. 3. (a) Experimental (circles) and fitted (lines) CO stretching band profile in liquid methanol. The relative intensities of the four Gaussian components are fixed to results of Fig. 2(b). Bands appearing at 1110 and 1160 cm^{-1} are symmetric and asymmetric δ(OCH) deformations [9]. (b) Frequencies of the CO stretching bands deduced from our model, symbol definitions as in previous figures. (c) Frequency at the maximum of the CO stretching band deduced from our experiments (full squares) and experimental data from Lemos and Camargo [10].

We summarize the frequencies under pressure obtained from our Gaussian fits in Fig. 3(b). Alternatively, if we plot the frequency of the peak maximum in a similar fashion to previous investigators, then the frequency exhibits a minimum at about 5 kbar, in agreement with Ref. [10]. We note that the frequencies of the four Gaussians can be considered constant at low pressures [Fig. 3(b)] and show a blueshift at pressures above 7–8 kbar. We can thus explain that the previously reported asymmetry in the profile of the CO stretching band is a consequence of the change in the concentration of the clusters induced by pressure [10]. Similarly, the apparent anomalous minimum in the CO stretch mode frequency is

TABLE I. Characteristics of the fit to CO stretching band compared to those from molecular beam experiments [17]. We expect the liquid frequencies to be about 9 cm^{-1} lower than those of the gas.

	Cluster	Ref. [17]	This work
Frequency (cm^{-1})	Dimer	1027.3–1029.6	(1018 ± 3)
		1046.4–1052.8	(1042 ± 2)
	Trimer	1040.6–1041.2	(1029 ± 2)
	Tetramer	1043.6–1045.1	(1037 ± 3)
FWHM (cm^{-1})	Dimer	19-36	(55 ± 8)
		29	(35 ± 5)
	Trimer	13–16	(15 ± 5)
	Tetramer	8–12	(15 ± 5)

not induced by complex hydrogen-bond effects, but is rather a reflection of the cluster concentration changes induced by pressure.

In summary, we have provided insight about cluster formation and hydrogen bonding in liquid methanol that explains a peculiar behavior not recognized before. The present results suggest that liquid methanol can be considered a mixture of molecular aggregates resembling the structure of two, three, and four-member clusters. This simple picture of liquid methanol is able to reconcile both structural (radial distribution function) and spectroscopic data at high pressure. In particular, Raman spectra at high pressure are interpreted by cooperative shifts observed for the OH and CO Raman bands of each cluster.

We believe that the current interpretation given for liquid methanol likely can be extended to other hydrogen-bonded systems, including water. This suggestion reinforces the conclusion put forth by Robinson *et al.* [31], that high-pressure Raman measurements on water might serve to elucidate the origin of the water anomalies [32], including those occurring in the radial distribution function as a function of temperature and pressure [33,34]. Our results indicate that future experiments on associated systems should be performed under high pressure to avoid continuous changes in the concentration of the clusters resulting under dilution conditions or as a function of temperature. Finally, the fact that compression promotes a pseudoequilibrium cluster concentration in the liquid that remains constant at high pressures suggests that the glass-transition mechanism in associated liquids might be explained within the frame of a mixturelike model [35].

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