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## Using the C–O stretch to unravel the nature of hydrogen bonding in low-temperature solid methanol-water condensates

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Transmission infrared spectroscopy has been used in a systematic laboratory study to investigate hydrogen bonding in binary mixtures of CH<sub>3</sub>OH and H<sub>2</sub>O, vapour deposited at 30 K, as a function of CH<sub>3</sub>OH/H<sub>2</sub>O mixing ratio, R. Strong intermolecular interactions are evident between CH<sub>3</sub>OH and H<sub>2</sub>O with infrared band profiles of the binary ices differing from that of the pure components and changing significantly with R. Consistent evidence from the O–H and C–H band profiles and detailed analysis of the C–O stretch band reveal two different hydrogen bonding structural regimes below and above R=0.6–0.7. The vapour deposited solid mixtures were found to exhibit behaviour similar to that of liquids with evidence of inhomogeneity and higher coordination number of hydrogen bonds that are concentration dependent. The C–O stretch band is found to consist of three components around 1039 cm<sup>-1</sup> ('blue'), 1027 cm<sup>-1</sup> ('middle') and 1011 cm<sup>-1</sup> ('red'). The 'blue' and 'middle' components corresponding to environments with CH<sub>3</sub>OH dominating as a proton donor (PD) and proton acceptor (PA) respectively reveal preferential bonding of CH<sub>3</sub>OH as a PA and H<sub>2</sub>O as a PD in the mixtures. The 'red' component is only present in the presence of H<sub>2</sub>O and has been assigned to the involvement of both lone pairs of electrons on the oxygen atom of CH<sub>3</sub>OH as a PA to two PD H<sub>2</sub>O atoms. Cooperative effects are evident with concurrent blue-shifts in the C–H stretching modes of CH<sub>3</sub>OH below R=0.6 indicating CH<sub>3</sub> group participation in hydrogen bonding.

### 1 Introduction

Solid methanol (CH<sub>3</sub>OH) is an important constituent of ices in the interstellar medium (ISM). It is the precursor for the formation of many of the complex organic molecules (COMs) observed in the ISM, both in the gas and the solid phases; molecules that subsequently became incorporated into cometary ices during the formation of planetary systems, with some believed to lead to the formation of prebiotic molecules responsible for the chemical origins of life<sup>1–4</sup>. CH<sub>3</sub>OH has been observed in comets<sup>5–7</sup> and on the surfaces of Trans-Neptunian objects<sup>8–10</sup>, that are believed to be preserved from the primordial cloud and planetary accretion disk that formed our Solar System. In dense molecular clouds, from which stars are formed, CH<sub>3</sub>OH is observed to be one of the most abundant constituents of ices after H<sub>2</sub>O and CO<sup>11–14</sup>. Theoretical and experimental evidence suggests that interstellar CH<sub>3</sub>OH forms exclusively in the condensed phase on the surfaces of dust grains in dense molecular clouds, via successive hydrogenation of CO<sup>15–20</sup>. However wide variations in the abundance

of solid CH<sub>3</sub>OH in the ISM are observed, ranging from 5 to 30% relative to H<sub>2</sub>O and there is still much ambiguity in determining CH<sub>3</sub>OH abundances and the degree of mixing with H<sub>2</sub>O due to the overlapping of observed CH<sub>3</sub>OH vibrational absorption bands with H<sub>2</sub>O and silicate absorption features.

The interpretation of observational infrared (IR) spectra of ices relies heavily on laboratory infrared absorption spectra of ice analogues grown under controlled experimental conditions. IR spectroscopy of molecular ices provides a powerful tool in the identification of species and interpretation of the structure and morphology of interstellar ices, since the IR spectra are highly sensitive to the ice temperature, composition, and mixing ratio of the molecular components, which are all intrinsically linked to the intermolecular interactions. Though a number of laboratory studies have been reported for the purposes of constraining methanol abundances from observational spectra<sup>21–26</sup>, detailed and systematic laboratory studies of mixtures/layers of solid H<sub>2</sub>O and CH<sub>3</sub>OH are still limited. Inspired by the need for such data to interpret observational spectra presented by Suutarinen *et al.*<sup>27</sup> we have carried out a detailed, systematic laboratory spectroscopic study of mixtures of vapour deposited CH<sub>3</sub>OH and H<sub>2</sub>O, at 30 K, as a function of CH<sub>3</sub>OH/H<sub>2</sub>O ratio. Whilst from an astro-

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nomical perspective, the shape and the intensity variations in the O–H and C–H stretching frequencies were sufficient to estimate CH<sub>3</sub>OH abundances in Suutarinen *et. al.*<sup>27</sup>, the CH<sub>3</sub>OH/H<sub>2</sub>O ratio could not be constrained and chemical knowledge is required to understand the significance of the spectral changes and link spectral bands, including the most indicative C–O stretch. Therefore this paper focuses not so much on the spectra, but what the spectra can inform us, from a chemical perspective, about the hydrogen bonding and intermixing of the two molecules, H<sub>2</sub>O and CH<sub>3</sub>OH, as a function of CH<sub>3</sub>OH dilution in H<sub>2</sub>O.

From a Physical Chemistry perspective, there has been considerable interest in CH<sub>3</sub>OH as it is the prototype molecule for hydrogen-bonding alcohols<sup>28</sup>. CH<sub>3</sub>OH, has attracted a lot of attention in both computational and experimental studies of hydrogen bonding and mixing in liquids, particularly with H<sub>2</sub>O. It is well known from laboratory and computational physical chemistry investigations that both CH<sub>3</sub>OH and H<sub>2</sub>O form strong hydrogen bonds both as pure constituents and in mixtures, interacting strongly with one another. Hydrogen bonding causes shifts in the vibrational frequencies of the functional groups that they are associated with and it is therefore possible to glean much about the structure and morphology of condensed ices from their infrared spectra. In CH<sub>3</sub>OH the vibrational spectra of the O–H, C–H and the C–O stretch are sensitive to the interaction between nearest neighbours. The interactions between CH<sub>3</sub>OH and H<sub>2</sub>O have been studied in mixed CH<sub>3</sub>OH/H<sub>2</sub>O liquids<sup>29–32</sup>, heterodimers<sup>33–35</sup> and small clusters both in the gas phase and in matrix isolation studies<sup>33,34</sup>, supported with extensive computational studies<sup>36–44</sup>. The O–H stretch has been used extensively to study hydrogen bonding between H<sub>2</sub>O and CH<sub>3</sub>OH in dimers, matrix isolation and in clusters, however, in the bulk condensed and liquid phases this poses a problem as the broad absorption bands due to the O–H stretching frequencies of both CH<sub>3</sub>OH and H<sub>2</sub>O overlap. Therefore to better understand the CH<sub>3</sub>OH...H<sub>2</sub>O interactions in the bulk solid phase, we focus our analysis in this paper on the C–O stretch of CH<sub>3</sub>OH.

The C–O stretch is also sensitive to hydrogen bonding, however, few studies have concentrated on this band<sup>31,32</sup>. It is a favourable band for the study of mixtures with H<sub>2</sub>O in the solid (and liquid) phase as it does not overlap with any of the H<sub>2</sub>O features and is therefore useful in the interpretation of astronomical spectra. However, observationally this band has not yet been exploited as it lies on a strong interstellar silicate absorption band<sup>21,22,45</sup> which until recently has been difficult to subtract. Nevertheless, in this paper we focus our attention primarily on the C–O stretch band of CH<sub>3</sub>OH and the effect the mixing ratio between CH<sub>3</sub>OH and H<sub>2</sub>O has on the band profile. We wish assess whether the C–O stretch band of CH<sub>3</sub>OH can be used as an observational tool to infer the degree of mixing in interstellar ices, particularly with higher sensitivity of newly emerging telescopes that would also enable the simultaneous observation of the C–O, C–H and O–H regions of the spectrum with a single telescope, such as the James Webb Space Telescope<sup>27</sup>. Therefore the primary focus of this paper is that, in order to better inform the Astronomy community, we wish to understand the physico-chemical nature of the intermolecular interactions within the bulk mixed CH<sub>3</sub>OH and H<sub>2</sub>O

low-temperature condensed ice films.

## 2 Experimental

The experiments were carried out using a high vacuum chamber, with a base pressure of  $1 \times 10^{-9}$  mbar. A 1.5 cm diameter infrared transmitting ZnSe substrate, mounted in a copper sample holder was cooled using a closed cycle helium cryostat (Sumitomo) to temperatures of 30 K. CH<sub>3</sub>OH (liquid, Sigma-Aldrich  $\geq 99.9\%$  HPLC grade) and H<sub>2</sub>O (liquid, triply distilled, deionised) samples were pre-mixed in the gas dosing line after three freeze-pump-thaw cycles. The gas line pressures were held below 10 mbar to avoid condensation of H<sub>2</sub>O. Ice films were grown by background filling the vacuum chamber and maintaining a pressure of  $1 \times 10^{-7}$  mbar during deposition using a needle valve to set the flow of gases into the chamber. Ices were grown at a rate of approximately  $0.1 \text{ ML s}^{-1}$  and all samples were around 100 nm thick as determined from the infrared spectra. Under these conditions the pressure drop in the gas line during deposition was negligible. The partial pressures in the gas line were used as a rough indicator of the sample ratios, however due to differences in the vapour pressure between CH<sub>3</sub>OH and H<sub>2</sub>O and adsorption-exchange processes on the stainless steel walls of the gas line, the final sample ratios did not entirely agree with the ratios of the pre-mixed gases. Therefore the exact ratios of the mixed ices were subsequently determined from the infrared spectra by calculating the column densities from the integrated absorbance of two bands of CH<sub>3</sub>OH and two bands of H<sub>2</sub>O, as described in Section 2.1. Infrared spectra of the CH<sub>3</sub>OH and H<sub>2</sub>O ice mixtures were measured using a Thermo Nicolet NEXUS FTIR spectrometer in the range  $4000\text{--}800 \text{ cm}^{-1}$  at  $1 \text{ cm}^{-1}$  resolution and averaging together 512 scans.

### 2.1 Determining the CH<sub>3</sub>OH/H<sub>2</sub>O ratio, R

The CH<sub>3</sub>OH:H<sub>2</sub>O ratios were determined by calculating the CH<sub>3</sub>OH and H<sub>2</sub>O column densities from the infrared absorption spectra. The column density  $N_i$  (molecules  $\text{cm}^{-2}$ ) of a molecular species  $i$  is determined using the Beer-Lambert Law:

$$I_t(\bar{\nu}) = I_0(\bar{\nu})e^{-\sigma_i(\bar{\nu})N_i} \quad (1)$$

where  $I_0(\bar{\nu})$  and  $I_t(\bar{\nu})$  are the incident and the transmitted intensities at wavenumber  $\bar{\nu}$  ( $\text{cm}^{-1}$ ) and  $\sigma_i(\bar{\nu})$  ( $\text{cm}^2$ ) is the absorption cross section for a given molecular species  $i$ .

Rearranging Equation 1, we get

$$\ln \left( \frac{I_0(\bar{\nu})}{I_t(\bar{\nu})} \right) = \tau(\bar{\nu}) = \sigma_i(\bar{\nu})N_i \quad (2)$$

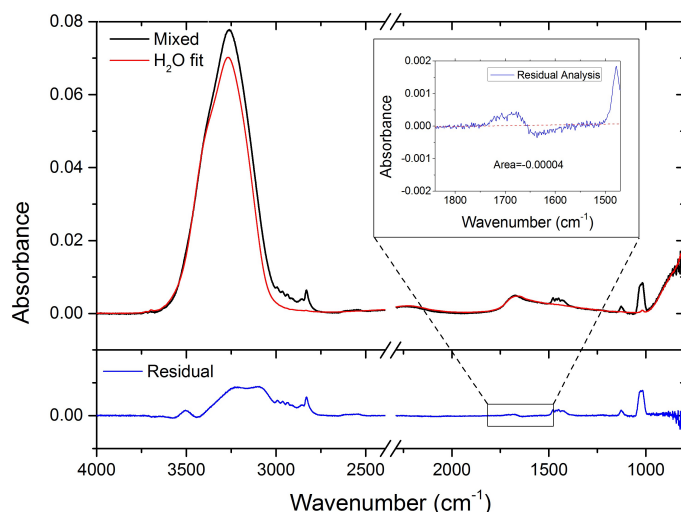
where  $\tau(\bar{\nu})$  is the optical depth as a function of frequency  $\bar{\nu}$  ( $\text{cm}^{-1}$ ) which is obtained from the absorbance (log scale) measured by the FTIR spectrometer and converted to optical depth (ln scale) by multiplying by  $\ln(10)$ .

Integrating Equation 2 over the absorption band for a given vibrational transition and rearranging, gives the column density

$$N_i = \frac{1}{A_i} \int \tau(\bar{\nu}) d\bar{\nu} \quad (3)$$

where the integral  $\int \tau(\bar{\nu})d\bar{\nu}$  corresponds to the area of the absorption band for a given vibrational mode of a molecular species  $i$  and  $A_i = \int \sigma_i(\bar{\nu})d\bar{\nu}$  (cm molecule<sup>-1</sup>) is the band strength or the integrated absorption coefficient for the particular absorption band that is a constant obtained from literature.

The CH<sub>3</sub>OH column densities were calculated from the integrated areas of two absorption bands: the C–O stretch band around 1025 cm<sup>-1</sup> and the symmetric C–H stretch band around 2828 cm<sup>-1</sup>, these were then compared and averaged. The C–O stretch was selected because of its high intensity and that it does not overlap with H<sub>2</sub>O bands except for the tail of the H<sub>2</sub>O libration mode around 760 cm<sup>-1</sup> (just outside of our spectral range), where a polynomial baseline was subtracted. The C–H stretch band was selected for comparison as its band strength is known to be largely independent of the effects of dilution with H<sub>2</sub>O<sup>25</sup>. However, errors in determining the area of the band arise due to the determination of the baseline, as it lies on the red wing of the combined water and methanol O–H stretch. Nevertheless, the column densities determined from each of the bands of methanol were within  $\pm 10\%$  of each other and an average of the two values was used for the final column density of CH<sub>3</sub>OH for each of our samples.



**Fig. 1** An example of the fitting process used to determine the H<sub>2</sub>O column density. A pure H<sub>2</sub>O spectrum is fitted to the mixed spectrum ( $R=0.16$  in this example) and subtracted such that the residual provides a flat baseline underneath all the CH<sub>3</sub>OH features, except the O–H stretch where there is severe overlapping and interaction between CH<sub>3</sub>OH and H<sub>2</sub>O, and that the sum of the positive and negative components are close to zero in the H<sub>2</sub>O bending region (an expanded region is shown in the inset).

The H<sub>2</sub>O column densities were calculated from the integrated areas of the two most intense bands in our spectral range: the O–H stretch band (around 3270 cm<sup>-1</sup>) and the O–H bend (around 1670 cm<sup>-1</sup>). However, it was not possible to directly measure the areas of these bands as they both overlap with CH<sub>3</sub>OH absorption features. The band areas were therefore determined by fitting a pure H<sub>2</sub>O spectrum to the mixed spectra, subtracting it from the mixed spectrum and examining the residual spectra around the region of the libration mode near the low frequency cut-off of our

spectral range, the combination modes ( $\sim 2200$  cm<sup>-1</sup>) and more specifically in the O–H bending region, as shown in Figure 1. Due to the strong interactions between CH<sub>3</sub>OH and H<sub>2</sub>O (discussed later), that give rise to shifts in band positions and changes in width, the residuals around the O–H bending mode region contained both positive and negative components. The fitting was thus iterated and the residuals minimised so that the sum of the positive and negative components in all regions except the O–H stretch where as close to zero as possible. The integrated band areas of the O–H stretch and the O–H bend bands in the fitted pure H<sub>2</sub>O spectrum were then used to calculate the H<sub>2</sub>O column densities, using linear baselines from 3900 to 2690 cm<sup>-1</sup> for the O–H stretch and from 1960 to 1060 cm<sup>-1</sup> for the O–H bend. Errors in the resulting water band areas were between a few % to 10% and the column densities determined from the two bands were found to be within  $\pm 5\%$  of each other.

The column densities  $N_{\text{CH}_3\text{OH}}$  and  $N_{\text{H}_2\text{O}}$  were then calculated from Equation 3. The integrated absorption coefficients or the 'A-values', as they are commonly referred to in the literature, for the four absorption bands were derived from reported values in the literature. A-values of  $2.0 \times 10^{-16}$  cm molecule<sup>-1</sup> and  $1.2 \times 10^{-17}$  cm molecule<sup>-1</sup> were used for the O–H stretch (near 3270 cm<sup>-1</sup>) and the O–H bend (near 1670 cm<sup>-1</sup>) bands of H<sub>2</sub>O respectively<sup>46</sup>. It is to be noted that there is considerable variation in the A-values reported<sup>11,25,26,47,48</sup> for the bands of methanol, with little consistent dependence on the mixing medium, within the error limits of up to 30%. We used averaged values of  $1.6 \times 10^{-17}$  cm molecule<sup>-1</sup> and  $5.6 \times 10^{-18}$  cm molecule<sup>-1</sup> for the C–O stretch and the symmetric C–H stretch bands of CH<sub>3</sub>OH respectively. The methanol column densities calculated using either the C–H stretch, the C–O stretch band or both were well within the errors introduced by the A-values. Furthermore, any errors introduced by the A-values would only produce a systematic shift in our data and therefore not affect the trends that we observe.

In the remainder of this paper we refer to the mixing ratio,  $R$ , between CH<sub>3</sub>OH and H<sub>2</sub>O as a ratio of their column densities, where

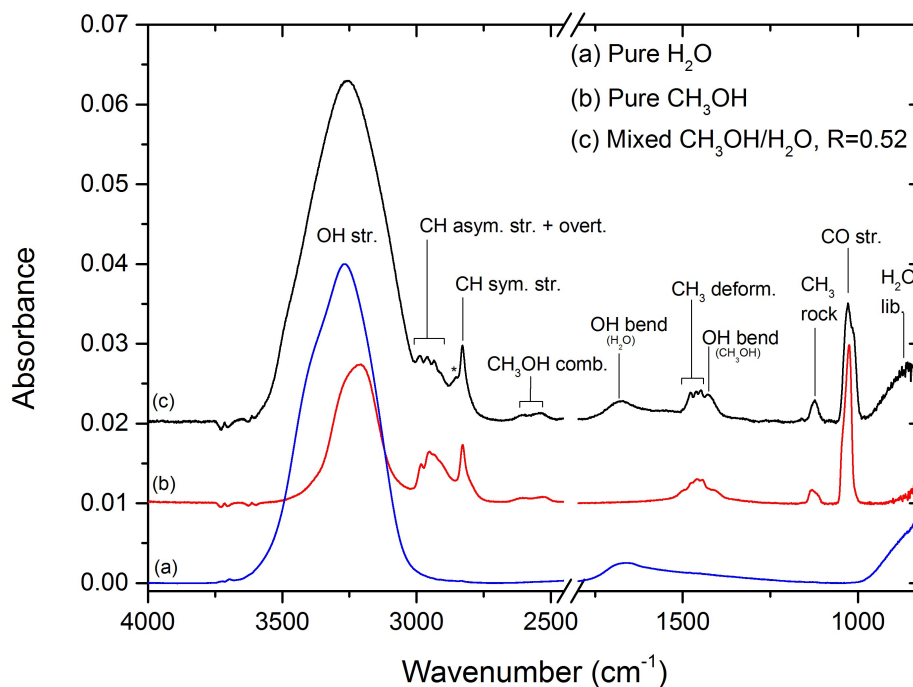
$$R = \frac{N_{\text{CH}_3\text{OH}}}{N_{\text{H}_2\text{O}}} \quad (4)$$

We have measured the infrared spectra of 18 samples of CH<sub>3</sub>OH/H<sub>2</sub>O at 30 K, with different relative concentrations as listed in Table 1.

### 3 Results and Discussion

#### 3.1 Comparison between pure and mixed CH<sub>3</sub>OH and H<sub>2</sub>O amorphous films

The spectra of the mixed CH<sub>3</sub>OH and H<sub>2</sub>O show considerable changes in the observed band profiles as a function of concentration and specific regions of the spectrum will be discussed in detail in the following sections with particular focus on the C–O stretch of CH<sub>3</sub>OH. However, we will initially briefly compare one example of a mixed CH<sub>3</sub>OH and H<sub>2</sub>O sample with  $R=0.52$  with that of pure CH<sub>3</sub>OH and H<sub>2</sub>O spectra prepared under the same conditions, as shown in Figure 2, in order to assign the bands (shown in Table 2) and introduce the various regions of the spec-



**Fig. 2** Comparison between the infrared spectra of (a) pure H<sub>2</sub>O, (b) pure CH<sub>3</sub>OH and an example of a mixed CH<sub>3</sub>OH/H<sub>2</sub>O sample with R=0.52 showing band assignments. The pure H<sub>2</sub>O and CH<sub>3</sub>OH spectra are normalised to the column densities of H<sub>2</sub>O and CH<sub>3</sub>OH that constitute the mixed sample.

**Table 2** Comparison between band positions of the pure CH<sub>3</sub>OH, H<sub>2</sub>O and one mixed R=0.52 sample shown in Figure 2. Band assignments are from (a) Hagen *et. al.*<sup>49</sup>, (b) Hänninen *et. al.*<sup>50</sup> and (c) Yuhnevich *et. al.*<sup>37</sup>. (sh)=shoulder

| Molecule           | Mode                 | Assignment               | Reference | Pure CH <sub>3</sub> OH<br>$\bar{\nu}$ cm <sup>-1</sup> | Pure H <sub>2</sub> O<br>$\bar{\nu}$ cm <sup>-1</sup> | Mixed R=0.52<br>$\bar{\nu}$ cm <sup>-1</sup> |
|--------------------|----------------------|--------------------------|-----------|---|---|--|
| H <sub>2</sub> O   | $\nu_1, \nu_3$       | O-H stretch              | a         |   | 3272  |  |
|                    | $\nu_2$              | O-H bend                 | a         |   | 1659  | 1673   |
|                    | $\nu_2 + \nu_L$      | Combination              | a         |   | 2213  | 2236   |
| CH <sub>3</sub> OH | $\nu_1$              | O-H stretch              | a, b      | 3208  |   |  |
|                    | $\nu_{2(a)}$         | C-H asym. stretch        | a, b      | 2983  |   | 2988   |
|                    | $\nu_{9(a)}$         | C-H asym. stretch        | a, b      | 2953  |   | 2960   |
|                    | $2\delta_a$          | CH <sub>3</sub> overtone | c         | 2932(sh)  |   | 2934   |
|                    | $2\delta_a$          | CH <sub>3</sub> overtone | c         | 2910(sh)  |   | 2910   |
|                    | $\nu_{3(s)}$         | C-H sym. stretch         | a, b      | 2828  |   | 2829   |
|                    | $\nu_6 + \nu_8$      | Combination              | a         | 2602  |   | 2603   |
|                    | $\nu_6 + \nu_9$      | Combination              | a         | 2527  |   | 2540   |
|                    | $\nu_4(\delta_a)$    | C-H bend                 | b, c      | 1475  |   | 1477   |
|                    | $\nu_{10}(\delta_a)$ | C-H bend                 | b, c      | 1458  |   | 1462   |
|                    | $\nu_5(\delta_s)$    | C-H bend                 | b, c      | 1444  |   | 1449   |
|                    | $\nu_6$              | O-H bend                 | a, b      | 1408 (sh)   |   | 1427   |
|                    | $\nu_7, \nu_{11}$    | CH <sub>3</sub> rock     | b         | 1131, 1117 (sh)   |   | 1123   |
|                    | $\nu_8$              | C-O stretch              | a, b      | 1025  |   | 1027, 1015 (sh)                              |
| mixed              |                      | overlapped O-H stretch   |           |   |   | 3258   |
|                    |                      | unassigned               |           |   |   | 2853   |

**Table 1** Mixing ratios of samples deposited at 30 K, as determined from the  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  column densities,  $N_{\text{CH}_3\text{OH}}$  and  $N_{\text{H}_2\text{O}}$  respectively, calculated from the infrared spectra as described in Section 2.1

| Mixing Ratio<br>$R = \frac{N_{\text{CH}_3\text{OH}}}{N_{\text{H}_2\text{O}}}$ | $N_{\text{CH}_3\text{OH}} \times 10^{16}$<br>(molec. $\text{cm}^{-2}$ ) | $N_{\text{H}_2\text{O}} \times 10^{16}$<br>(molec. $\text{cm}^{-2}$ ) |
|---|---|---|
| 0.0055 ± 0.0005   | 0.13 ± 0.01   | 23.07 ± 1.63  |
| 0.14 ± 0.01   | 3.21 ± 0.17   | 22.91 ± 1.62  |
| 0.16 ± 0.01   | 3.99 ± 0.21   | 25.02 ± 1.77  |
| 0.22 ± 0.02   | 5.00 ± 0.26   | 22.67 ± 1.60  |
| 0.38 ± 0.03   | 8.58 ± 0.43   | 22.62 ± 1.60  |
| 0.52 ± 0.04   | 7.52 ± 0.37   | 14.58 ± 1.03  |
| 0.62 ± 0.05   | 9.40 ± 0.46   | 15.19 ± 1.07  |
| 0.67 ± 0.06   | 10.43 ± 0.51  | 15.66 ± 1.11  |
| 0.74 ± 0.07   | 6.29 ± 0.33   | 8.48 ± 0.60   |
| 1.00 ± 0.08   | 7.57 ± 0.38   | 7.59 ± 0.44   |
| 1.14 ± 0.09   | 7.64 ± 0.39   | 6.71 ± 0.40   |
| 1.24 ± 0.11   | 7.20 ± 0.36   | 5.80 ± 0.41   |
| 1.48 ± 0.13   | 8.48 ± 0.42   | 5.72 ± 0.40   |
| 1.64 ± 0.14   | 8.84 ± 0.43   | 5.38 ± 0.38   |
| 1.78 ± 0.15   | 13.28 ± 0.64  | 7.46 ± 0.53   |
| 1.90 ± 0.16   | 12.00 ± 0.56  | 6.30 ± 0.45   |
| 2.31 ± 0.20   | 9.80 ± 0.47   | 4.24 ± 0.30   |
| 2.83 ± 0.24   | 11.81 ± 0.56  | 4.17 ± 0.29   |
| Pure $\text{CH}_3\text{OH}$   | 22.42 ± 0.14  |   |

trum that will be referred to throughout the remainder of this paper. It is obvious from Figure 2 that the features in the infrared spectrum of the mixed example sample differ significantly from those of the spectra of the pure constituents. This is clear indication that there is considerable interaction between the  $\text{CH}_3\text{OH}$  and the  $\text{H}_2\text{O}$  molecules within the mixed ice matrix.

The most intense band in the spectrum is due to overlapping O–H stretching modes of  $\text{CH}_3\text{OH}$  ( $\nu_1$ ) and  $\text{H}_2\text{O}$  ( $\nu_1$ ,  $\nu_2$ ) around  $3260 \text{ cm}^{-1}$ . In the mixed ice this band is visibly broadened and its peak maximum is red-shifted with respect to pure  $\text{H}_2\text{O}$  and blue-shifted with respect to pure  $\text{CH}_3\text{OH}$ . Changes in the frequency of the O–H stretching mode in both  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  components are indicative of hydrogen bonding. This band exhibits changes in width and position as a function of  $R$  as will be discussed in Section 3.2. The O–H bending band ( $\nu_2$ ) of  $\text{H}_2\text{O}$  that peaks at  $1659 \text{ cm}^{-1}$  in pure  $\text{H}_2\text{O}$  appears slightly narrowed and blue-shifted in the mixed sample. Blueshifts in the O–H bending mode are indicative of strong hydrogen bonding. A further blue-shift in the presence of  $\text{CH}_3\text{OH}$  might therefore suggest stronger  $\text{CH}_3\text{OH} \cdots \text{H}_2\text{O}$  hydrogen bonding than  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ . In fact  $\text{CH}_3\text{OH} \cdots \text{H}_2\text{O}$  binding energy is reported to be higher than that for both  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$  and  $\text{CH}_3\text{OH} \cdots \text{CH}_3\text{OH}$ <sup>51</sup>.

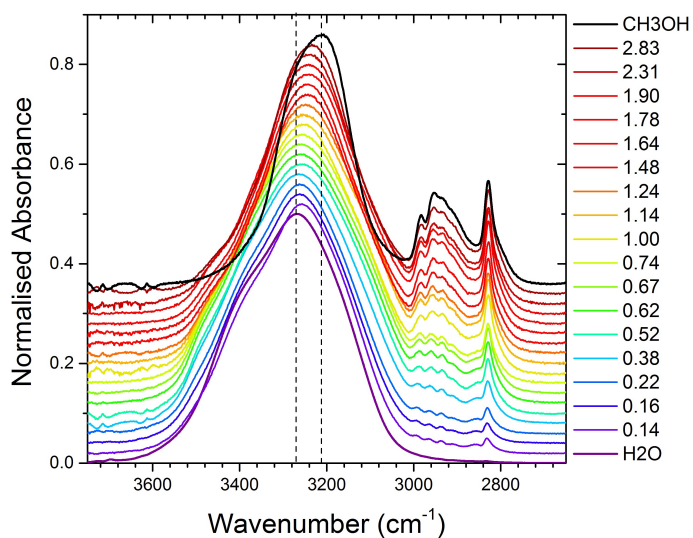
The C–H stretching region of  $\text{CH}_3\text{OH}$  lies on the red wing of the O–H stretch band between  $2700$  and  $3020 \text{ cm}^{-1}$ . There is a slight blue-shift in the symmetric C–H stretch band ( $\nu_{3(s)}$ ) around  $2829 \text{ cm}^{-1}$  and a shoulder appears around  $2853 \text{ cm}^{-1}$  that is only present in mixtures with  $\text{H}_2\text{O}$ . It is also interesting to note that the asymmetric C–H stretch region that appears as a broad bumpy feature in pure  $\text{CH}_3\text{OH}$ , exhibits four distinct peaks around  $2990$ ,  $2960$ ,  $2935$  and  $2910 \text{ cm}^{-1}$  in the mixed sample, indicating a separation of the two asymmetric stretching modes ( $\nu_{2(a)}$  and  $\nu_{9(a)}$ ) and the two overtone bending modes ( $2\delta_s$ ). As with the O–H stretch, the C–H stretch bands exhibit a change in position and width as a function of mixing ratio,  $R$ . A more detailed discussion

of this region follows in section 3.3.

The  $\text{CH}_3$  bending modes ( $\nu_4$ ,  $\nu_5$  and  $\nu_{10,s}$ ) of  $\text{CH}_3\text{OH}$  lie on the red wing of the  $\text{H}_2\text{O}$  O–H bending band between  $1300$  and  $1550 \text{ cm}^{-1}$ . Similarly to the C–H stretching modes, the C–H bending modes overlap and appear as a broad feature in pure  $\text{CH}_3\text{OH}$ , but the four modes become better defined and blue-shift in the mixed samples. Around  $1130 \text{ cm}^{-1}$ , the  $\text{CH}_3$  rocking mode band consists of two broad components ( $\nu_7$  and  $\nu_{11}$ ) in pure  $\text{CH}_3\text{OH}$ , but only a single peak is evident in the mixed sample around  $1123 \text{ cm}^{-1}$ . The C–O stretch band ( $\nu_8$ ) of  $\text{CH}_3\text{OH}$  appears as a sharp, slightly asymmetric peak around  $1027 \text{ cm}^{-1}$  in pure  $\text{CH}_3\text{OH}$ . However, in the mixed sample this band is red-shifted and exhibits a low frequency shoulder. The C–O stretch of  $\text{CH}_3\text{OH}$  is very sensitive to the interaction between  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  and shows a progressive change in profile as a function of  $\text{CH}_3\text{OH}$  concentration. A detailed analysis of this band follows in Section 3.4.

### 3.2 The O–H stretch

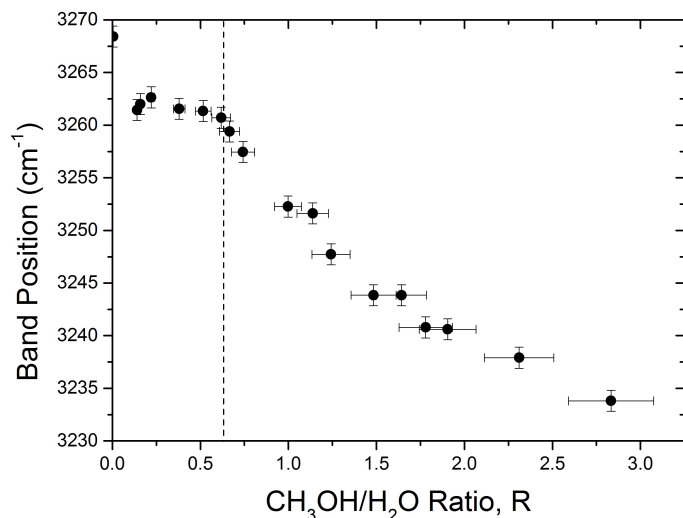
The complexity in analysing the O–H stretch band in mixtures of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  lies in the fact that the O–H stretch of  $\text{CH}_3\text{OH}$  and the O–H stretch of  $\text{H}_2\text{O}$  completely overlap. Figure 3 shows



**Fig. 3** The O–H stretch and the C–H stretch region of mixed  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  samples at 30 K, for different mixing ratios,  $R$ . Spectra are normalised to the peak intensity of the O–H stretch band and offset equally by 0.02 for clarity. The dotted lines indicate the positions of the pure  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  O–H stretch bands (spectra represented with thicker lines).

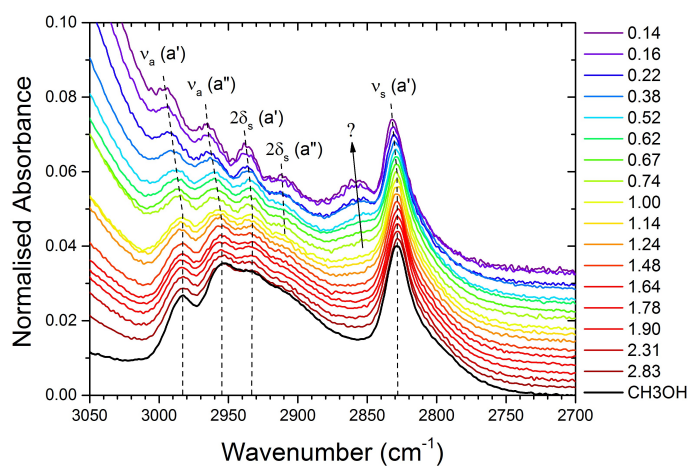
the effect of  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  ratio on the O–H stretch band (and the  $\text{CH}_3\text{OH}$  C–H stretching region, which will be discussed separately in Section 3.3). There is a progressive red-shift in the peak position of the combined O–H stretch band from that of pure  $\text{H}_2\text{O}$  at  $3268 \text{ cm}^{-1}$  to that of pure  $\text{CH}_3\text{OH}$  at  $3210 \text{ cm}^{-1}$  with increasing  $R$ . The position of the peak maximum is plotted as a function of  $R$  in Figure 4 and can be seen to progressively red-shift with increasing  $R$ . However the slope of the shift as a function of  $R$  changes gradient around  $R=0.6$

A certain degree of shifting is expected as the O–H stretch



**Fig. 4** The O–H stretch peak position of mixed CH<sub>3</sub>OH/H<sub>2</sub>O samples as a function of mixing ratio, R. There is a clearly a change in gradient around R=0.6, as highlighted with the dashed vertical line, that is indicative of two different bonding environment regimes.

band is composed of the O–H stretching contributions from both species, where the pure components have different band maxima, so as the relative intensity of the CH<sub>3</sub>OH and H<sub>2</sub>O components change as a function of R, so will the resulting peak position, and the measured peak will lie somewhere between that of pure CH<sub>3</sub>OH and H<sub>2</sub>O. As expected, therefore the position of the band maxima in the mixtures are always blue-shifted with respect to the pure CH<sub>3</sub>OH and red-shifted with respect to pure H<sub>2</sub>O band positions. It is intriguing however, looking at Figure 4 that shows the change in band position as a function of R, that there is clearly an abrupt change in gradient at R=0.6. So the shift in the composite band maximum position in the mixed samples cannot be accounted for by the 'summation' effect of the pure constituents alone. In fact, looking at Figure 1 showing an example of a pure H<sub>2</sub>O spectrum subtracted from the spectrum of a mixed sample, the O–H stretch region in the residual spectrum does not resemble the O–H stretch of pure CH<sub>3</sub>OH after the H<sub>2</sub>O O–H stretch band is subtracted. The picture is certainly complicated by the hydrogen bonding interaction between CH<sub>3</sub>OH and H<sub>2</sub>O. The general red-shift in the O–H stretching frequency of H<sub>2</sub>O with the progressive addition of CH<sub>3</sub>OH (with increasing R) indicates stronger H<sub>2</sub>O proton donating hydrogen bonds as the O–H bond lengthens and weakens, also corroborated by the blue-shift in the H<sub>2</sub>O O–H bending mode as hydrogen bonding suppresses the bending mode. However this does not explain the change in gradient around R=0.6 in Figure 4. There clearly appears to be a physical change in the way the molecules bond to each other in the mixed samples, with two different regimes apparent below and above R=0.6. The reason for this will become apparent in the analysis of the C–O stretch band in Section 3.4, henceforth we make no further detailed analysis of the O–H band in this paper.

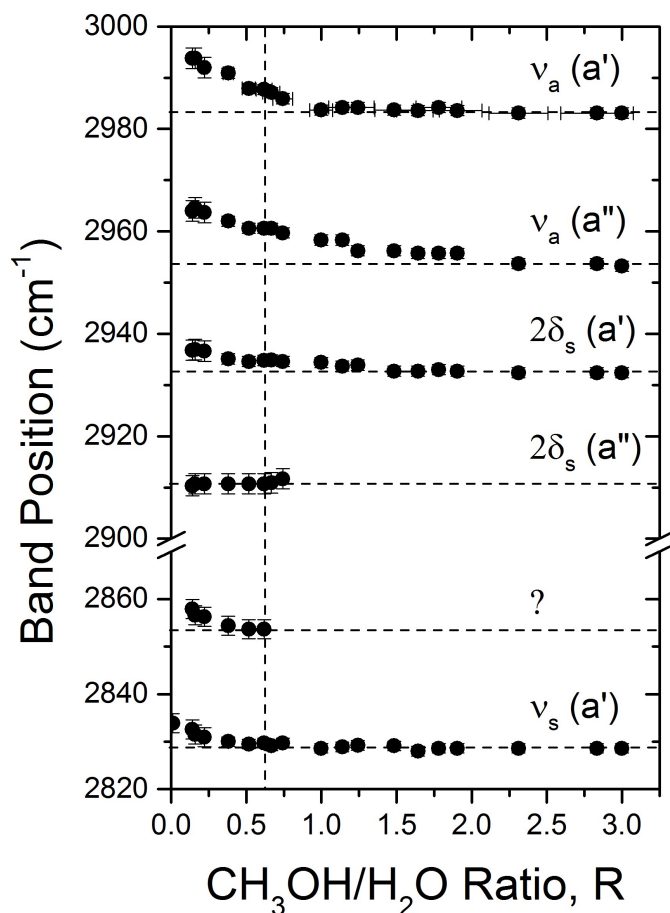


**Fig. 5** The C–H stretch region in mixed CH<sub>3</sub>OH/H<sub>2</sub>O samples at 30 K for different mixing ratios, R. Spectra are normalised to the maximum of the symmetric C–H stretch band ( $\nu_s$ ), offset equally by 0.02 and compared with pure CH<sub>3</sub>OH (spectrum indicated with a thicker line). Vertical guides show the evolution of the features with R, clearly showing a blue-shift in the band positions with increasing dilution of CH<sub>3</sub>OH in H<sub>2</sub>O. A new and yet unassigned feature appears at higher H<sub>2</sub>O concentrations (lower R) at around 2858 cm<sup>-1</sup> (indicated with a vertical arrow). Band assignments are from Yuhknevich *et. al.*<sup>37</sup>

### 3.3 The C–H stretch region

There is a progressive blue-shift in the symmetric ( $\nu_a$ ) and asymmetric ( $\nu_s$ ) C–H stretch bands of CH<sub>3</sub>OH with increasing dilution in H<sub>2</sub>O, as can be seen in Figure 5, but little to no shifting is observed in the overtone bands ( $2\delta_a$ ). The blue-shift appears to be more pronounced in the asymmetric stretch bands than the symmetric C–H stretch. The band positions in the C–H stretch region are plotted as a function of CH<sub>3</sub>OH/H<sub>2</sub>O ratio as shown in Figure 6. It is interesting to note that the onset of the blue-shift in the C–H stretch bands and the appearance of a new band around 2855 cm<sup>-1</sup> occurs below R=0.6–0.7. This is consistent with the position where the gradient changes in the O–H stretch position as a function of concentration in Figure 4, thus supporting the hypothesis that there are two different hydrogen-bonding regimes. Shifts in the C–H stretching frequencies would suggest that they are involved, either directly or indirectly, in bonding.

There are mixed views in the literature about the role of the CH<sub>3</sub>OH methyl group in bonding. In some cases it is considered hydrophobic and thus not involved in intermolecular interactions with either neighbouring CH<sub>3</sub>OH or H<sub>2</sub>O molecules<sup>30,32,36,52</sup>. In fact this appears to be the view held in the astronomy community where the role of the methyl group in intermolecular interactions is generally neglected. While in clusters, thin (monolayer) films and in the gas phase the methyl group shows hydrophobic behaviour, there has also been much discussion in the physical chemistry literature about the so-called 'blue-shifting' hydrogen bonds, with evidence to suggest that the C–H hydrogens in the methyl group of CH<sub>3</sub>OH in liquids do indeed take part in bonding<sup>37,38,53–55</sup> and that the weak bonds formed between the methyl hydrogens and an oxygen on the neighbouring CH<sub>3</sub>OH or H<sub>2</sub>O, are indeed considered to be true hydrogen bonds<sup>56,57</sup>. These bonds are associated with characteristic blue-shifts in the



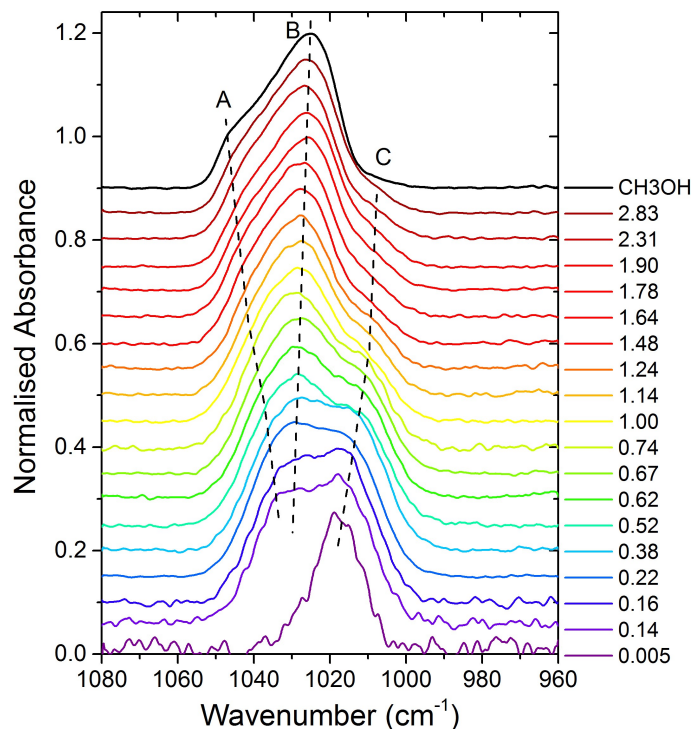
**Fig. 6** Band positions in the C-H stretch region of mixed  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  samples as a function of mixing ratio,  $R$ , clearly showing a more pronounced blue-shift in the asymmetric bands  $\nu_a$ , and asymmetric  $\nu_a$ , stretch bands and a slight blue-shift in one of the  $2\delta_s$  overtone bands. A new yet unassigned band (?) appears below  $R=0.6$ . Band assignments are from Yuhnevich *et. al.*<sup>37</sup>

C-H stretching frequency. Therefore, not unlike the liquid phase, in the bulk amorphous solid it is highly likely that the methyl group does indeed participate in hydrogen bonding. Thus the increasing blue-shift in the C-H bands below  $R=0.6-0.7$  that we see in Figures 5 and 6 strongly suggest that the methyl group begins to form hydrogen bonds, most likely with  $\text{H}_2\text{O}$  molecules due to higher  $\text{H}_2\text{O}$  concentrations at low  $R$ . Interestingly this is also around the mixing ratio where we hypothesise the change in the bonding environment observed in Figure 4 showing the variation in the O-H stretch position as a function of  $R$ . The splitting of the C-H stretch region in the mixed samples into four distinct bands compared to that of the less defined region in pure  $\text{CH}_3\text{OH}$  in fact suggests that only one  $\text{CH}_3$  hydrogen participates in a hydrogen bond<sup>37</sup>. This may also explain the comparatively smaller blue-shift of the symmetric stretch band ( $\nu_s$ ) compared to the asymmetric bands ( $\nu_a$ ). In order to fully understand the nature of interaction between  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ , especially at low  $\text{CH}_3\text{OH}$  concentrations, we focus our attention on the C-O stretch of  $\text{CH}_3\text{OH}$  in the following section. The C-O bond is the bridge between the  $\text{CH}_3$  and the OH ends of the  $\text{CH}_3\text{OH}$  molecule and is

therefore sensitive to changes in electron density resulting from hydrogen bonding, and will thus provide further insight into the nature of hydrogen bonding as a function of  $R$ .

### 3.4 The C-O stretch of $\text{CH}_3\text{OH}$

#### 3.4.1 C-O band spectral features.



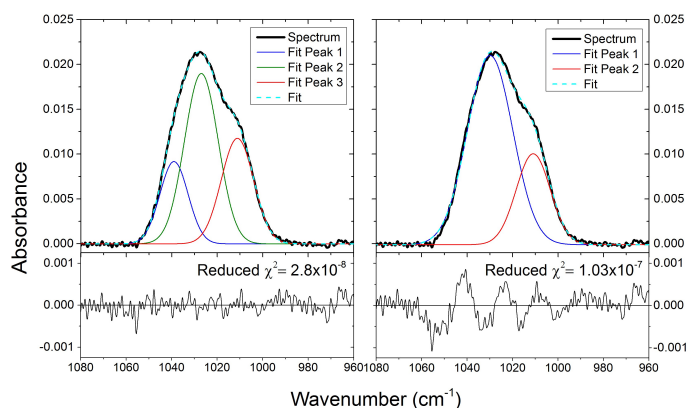
**Fig. 7** Evolution in the C-O stretching band profile with varying  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  concentration, compared with that of pure  $\text{CH}_3\text{OH}$ . This band clearly consists of three sub-components indicated with dashed lines and labelled A, B and C, with the 'red' component, C, that is uniquely present in the presence of  $\text{H}_2\text{O}$

Figure 7 shows the spectra of the C-O stretch of  $\text{CH}_3\text{OH}$  for different mixing ratios,  $R$ . In pure  $\text{CH}_3\text{OH}$  this band is asymmetric, peaking at around  $1025\text{ cm}^{-1}$ . The asymmetry of the band suggests the presence of sub-components. This becomes more apparent as the mixing ratio,  $R$ , is altered (as seen in Figure 7), suggesting that the subcomponents of the C-O stretching band are also related to the broader global changes occurring in the ice bonding and structure, and is indicative that, as we previously hypothesised, the C-O band is a reliable measure of the hydrogen bonding network in mixed  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  ices.

Notably, compared to the band profile of pure  $\text{CH}_3\text{OH}$ , a red shoulder appears in mixtures containing  $\text{H}_2\text{O}$ , that grows in intensity with increasing  $\text{H}_2\text{O}$  concentration (decreasing  $R$ ). In the very dilute  $\text{CH}_3\text{OH}$  sample ( $R=0.005$ ), this 'red component', peaking at  $1017\text{ cm}^{-1}$ , appears to be the dominant feature. Shifts of the C-O stretch as a function of concentration have been reported in literature, for example, Schutte *et.al.* reported C-O stretch peak positions of  $1018$  and  $1028\text{ cm}^{-1}$  for  $R=0.05$  and  $R=0.67$  respectively, in  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  mixtures deposited at  $10\text{ K}$ <sup>22</sup>. The presence of subcomponents have also been reported,



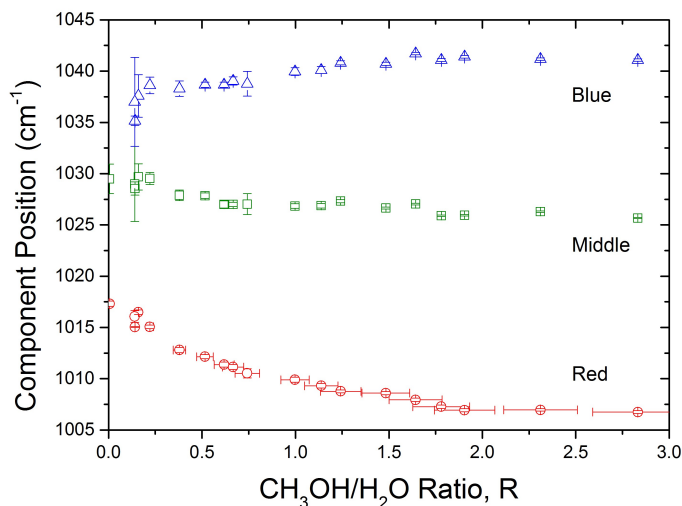
for example Ahmed *et. al.* report a shift from  $1015\text{ cm}^{-1}$  to  $1022\text{ cm}^{-1}$  in going from 0.1 to 0.9 mole fraction in liquid mixtures of  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  and attributed this to the presence of four sub-components at (i)  $1060$ , (ii)  $1023$ , (iii)  $1010$  and (iv)  $1000\text{ cm}^{-1}$ , assigned to different combinations of hydrogen bonding within the liquid: (i)  $\text{CH}_3\text{OH}$  H bonded with either  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{OH}$ , (ii) both O and H simultaneously bonded to two  $\text{CH}_3\text{OH}$  molecules, (iii) both O and H simultaneously bonded to two  $\text{H}_2\text{O}$  molecules and (iv) with  $\text{CH}_3\text{OH}$  O bonded to either  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{OH}$ , respectively<sup>32</sup>. Similarly, Bahr *et. al.* have reported the presence of three components at (i)  $1048$ , (ii)  $1034$  and (iii)  $1015\text{ cm}^{-1}$  in the RAIRS spectra of the C–O stretch of  $\text{CH}_3\text{OH}$  adsorbed onto amorphous solid water at  $121\text{ K}$ <sup>51</sup>. The authors assign the bands to (i) multilayer  $\text{CH}_3\text{OH}\cdots\text{CH}_3\text{OH}$  bonds, (ii) interaction of  $\text{CH}_3\text{OH}$  with the  $\text{H}_2\text{O}$  surface and (iii) the interaction of  $\text{CH}_3\text{OH}$  with both the  $\text{H}_2\text{O}$  surface and the first complete layer of  $\text{CH}_3\text{OH}$ , respectively.



**Fig. 8** An example of three and two Gaussian fits to the C–O stretch of  $\text{CH}_3\text{OH}$  for a sample with  $\text{CH}_3\text{OH}/\text{H}_2\text{O}=0.67$ . Corresponding residuals are shown below each graph together with the respective reduced  $\chi^2$  values from the fit.

In order to investigate the apparent subcomponents in our data and understand their physical significance, we have fitted the C–O stretching band with a linear combination of Gaussian functions. Gaussian functions were found to provide the best fits to the band profile over Lorentzian or Voigt functions. Indeed the Gaussian oscillator model is appropriate for absorption bands in strongly bonding disordered amorphous solids within which the intermolecular interactions give rise to a random distribution of bond lengths and angles. Thus each vibrational band is composed of a normal distribution of oscillators centred around an average peak frequency. Three Gaussians were fitted to the C–O stretch band of  $\text{CH}_3\text{OH}$ , one representing each clear component: two that are present in pure  $\text{CH}_3\text{OH}$  and a third that fits the red shoulder in the mixed samples. It was difficult to fit three components at low  $R$  values where the peak positions of the two 'pure  $\text{CH}_3\text{OH}$ ' components appear to converge, as can be seen in Figure 7 (dashed lines A and B). In these cases both a two- and a three-component fit were computed, and although the general results were commensurate with each other, in all cases the errors and the  $\chi$ -squared values were lower in the three-component fit as

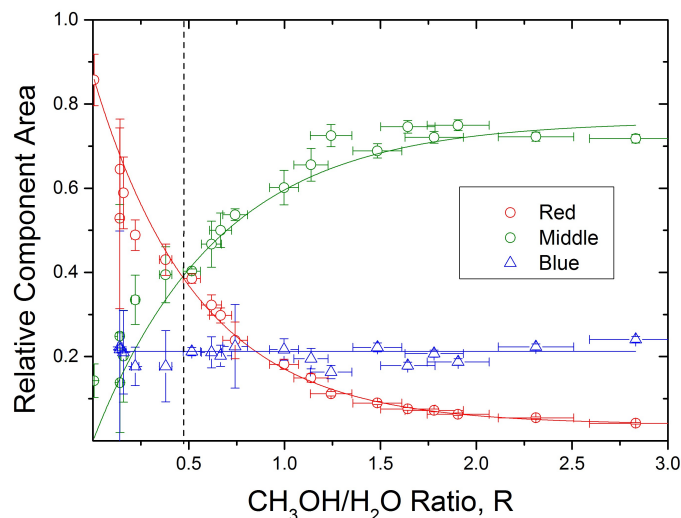
can be seen in the example shown in Figure 8 for  $R=0.67$ . Therefore for the remainder of this paper we discuss the C–O stretch band in terms of three sub-components, a 'red', 'blue' and 'middle' component.



**Fig. 9** The change in the peak position of three components, as derived from the Gaussian fits, of the C–O stretch band of  $\text{CH}_3\text{OH}$  as a function of  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  ratio.

The results of the Gaussian fits confirm that the C–O stretch of  $\text{CH}_3\text{OH}$  mixed in  $\text{H}_2\text{O}$  comprises of the three sub-components: A 'blue' component that shifts from  $1037\text{ cm}^{-1}$  to  $1041\text{ cm}^{-1}$ , a 'middle' component that shifts from  $1029\text{ cm}^{-1}$  to  $1025\text{ cm}^{-1}$ , and a 'red' component that shifts from  $1017\text{ cm}^{-1}$  to  $1007\text{ cm}^{-1}$  with increasing  $R$ . Figure 9 clearly shows the greatest variability in peak position occurs in the red component, which is red-shifted with increasing  $R$  indicating that the C–O bond is weakening in the associated ice environment as the  $\text{CH}_3\text{OH}$  concentration increases. Conversely, the blue and middle components show significantly less positional alteration, but diametrically opposite behaviour, with the middle (green) component slightly red-shifting with increasing  $R$  whilst the blue component is increasingly blue-shifted, indicating strengthening of the electron density in the C–O bond in this environment.

It is obvious from Figure 7 that not only the sub-component positions but also their intensities are changing with  $R$ . Therefore it may be more informative to investigate how the area of the fitted components, relative to the total band area, change as a function of  $R$ . This is illustrated in Figure 10. It can clearly be seen that, within the error bars, the relative area of the blue component remains independent of the  $\text{CH}_3\text{OH}$  concentration and constitutes about 21% of the total band area. However, the relative area of the red component decreases as the relative area of the middle component increases, crossing over around  $R=0.5$  (indicated with a dashed line in Figure 10). In fact, plotting the normalised area of the middle component against the normalised area of the red component, (shown in Figure 11), shows that they are inversely related, yielding a linear fit with a gradient that is very near to 1. Incidentally, at  $R=0.5$  stoichiometry dictates that there are two  $\text{H}_2\text{O}$  molecules to every  $\text{CH}_3\text{OH}$  molecule where the red

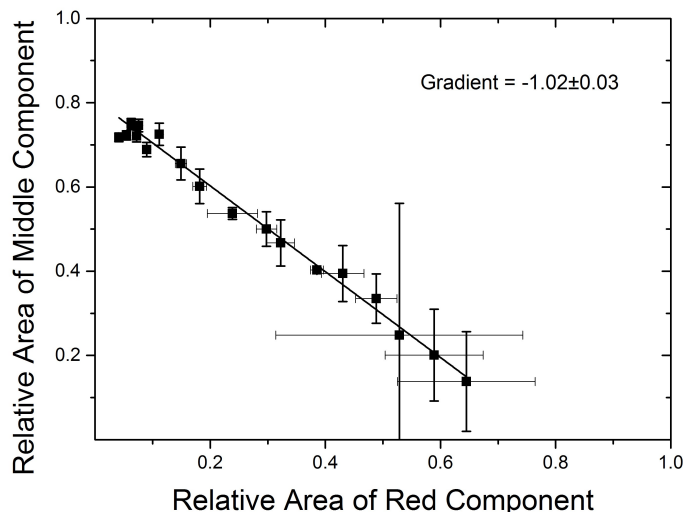


**Fig. 10** The variation of the band areas (relative to the total band area) of the three components of the C–O stretch band of  $\text{CH}_3\text{OH}$ , as derived from the Gaussian fits, as a function of  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  ratio,  $R$ .

and middle components cross and it would appear that the environment that gives rise to the middle component for  $R > 0.5$  is directly replaced with an environment that gives rise to the red component for  $R < 0.5$ . Therefore, it would appear that for every ice mixture there are at least two (and sometimes three) bonding environments, the question is what are they? We attempt to answer this in the next section.

### 3.4.2 $\text{CH}_3\text{OH}$ as a proton donor/acceptor.

Clearly the red component of the C–O stretch band of  $\text{CH}_3\text{OH}$  is only present in the presence of  $\text{H}_2\text{O}$ . But what structural orientations explain the blue and middle C–O stretch spectral features? Experimental and computational studies of  $\text{CH}_3\text{OH}$  dimers have shown that the infrared spectrum of the C–O stretch is comprised of two peaks, one red-shifted (by  $-6.8 \text{ cm}^{-1}$ ) and one blue-shifted (by  $+18.5 \text{ cm}^{-1}$ ) from the C–O stretching mode of the monomer around  $1033.5 \text{ cm}^{-1}$ <sup>58</sup>. These peaks have been attributed to the  $\text{CH}_3\text{OH}$  molecule acting as a proton acceptor (PA) and a proton donor (PD) respectively. When the molecule acts as a PA via the lone pairs of electrons on the O atom, the attractive hydrogen bond draws the electron density away from the C–O bond, resulting in an elongation of the bond and hence a red-shift in the vibrational frequency. Conversely, when the molecule acts as a PD, the coupling to the O–H bond results in a shortening in the C–O bond length, hence a blue-shift in the vibrational frequency. In our data, the shift of around  $+4$  to  $+8 \text{ cm}^{-1}$  in the blue component position and around  $-5$  to  $-9 \text{ cm}^{-1}$  in the middle component compared to the C–O stretching frequency of a free  $\text{CH}_3\text{OH}$  molecule could therefore be regarded as  $\text{CH}_3\text{OH}$  molecules acting as PA and PD respectively within the amorphous ice matrix. While splitting into distinct components within a solid requires symmetric coupling and long range order, such as in crystalline solids, within the bulk of an amorphous solid some molecules will simultaneously act as both PA and PD and some incomplete bonding is expected with free dangling-H bonds and un-



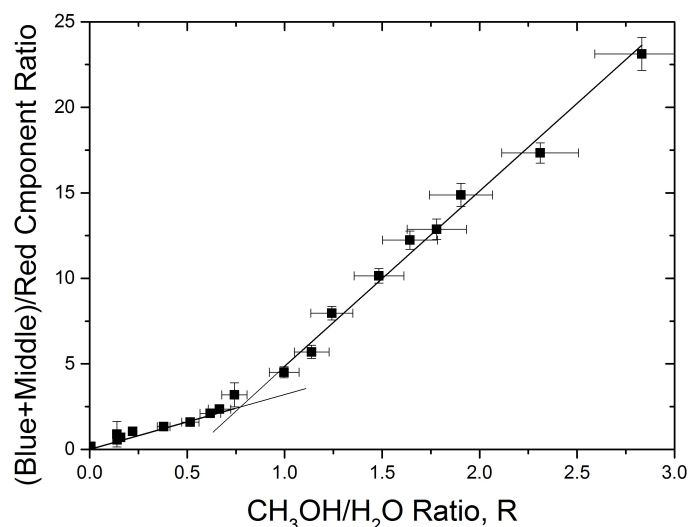
**Fig. 11** Relative area of the middle component versus the relative area of the red component, showing inverse linear correlation between the two components. The slope of the fitted line is  $-1.02 \pm 0.03$  and a Pearson's correlation coefficient of  $-0.99378$ .

bonded O lone pairs, providing a range of C–O stretch oscillator strengths, some short range order is expected essentially forming short chains, branches and cyclic structures. Nevertheless, what we observe in our spectra is the sum of the cooperative effects within the statistical distribution of bonding and non-bonding environments clearly giving rise to two broad components that can be distinguished, based on shifts in the vibrational frequency, into a blue-shifted PD dominated environment (blue component) and a red-shifted PA dominated environment (middle component).

Now let us consider what happens when  $\text{CH}_3\text{OH}$  is diluted in  $\text{H}_2\text{O}$ . Both the middle and the blue components of the C–O stretch are present as  $R$  decreases, however as seen in Figure 10, the blue component area remains more or less constant relative to the total C–O stretch band area. Therefore, it would appear that the presence of  $\text{H}_2\text{O}$  environment has little effect on the  $\text{CH}_3\text{OH}$  PD hydrogen bonds. It has been reported in literature<sup>33–35,39,58</sup> that gas phase and matrix isolated heterodimers of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  preferentially and *exclusively* bond with the  $\text{CH}_3\text{OH}$  acting as a PA and the  $\text{H}_2\text{O}$  as PD. Within an amorphous solid where a random arrangement of molecules and hydrogen bonded configurations are likely, it is still possible that during deposition there is preferential adsorption of  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  in the  $\text{CH}_3\text{OH}(\text{PA}) \cdots \text{H}_2\text{O}(\text{PD})$  arrangement. In fact, the observed blue-shift in the O–H bending mode and a red-shift in the O–H stretching mode of  $\text{H}_2\text{O}$  with increasing  $\text{CH}_3\text{OH}$  concentration (Figure 4) is also consistent with this picture. It is also interesting to note that in this arrangement, with  $\text{CH}_3\text{OH}$  acting as a PA when bonded to  $\text{H}_2\text{O}$  acting as a PD, no significant change in the O–H bond length of  $\text{CH}_3\text{OH}$  is reported<sup>33,58</sup>. Therefore with this picture in mind, that  $\text{CH}_3\text{OH}$  molecules are most likely to act as a PA to  $\text{H}_2\text{O}$  with increasing  $\text{H}_2\text{O}$  concentration (decreasing  $R$ ), it would stand to reason that the blue PD C–O stretch component of  $\text{CH}_3\text{OH}$  would thus remain unaffected, as our results show.

While the blue C–O stretch component (corresponding to a PD

CH<sub>3</sub>OH) appears to be constant, the middle component (corresponding to a PA CH<sub>3</sub>OH environment) appears to decrease with increased H<sub>2</sub>O concentration (decreasing R) and be directly replaced by the red component (Figure 11), thus suggesting that the latter must also relate to a PA environment and be directly associated with H<sub>2</sub>O concentration. However, *ab initio* calculations show that there is only a small difference between the relative binding strength of the CH<sub>3</sub>OH(PA)···CH<sub>3</sub>OH(PD) and the CH<sub>3</sub>OH(PA)···H<sub>2</sub>O(PD) hydrogen bonds<sup>39</sup>. Thus replacing a CH<sub>3</sub>OH donor molecule with a H<sub>2</sub>O donor molecule at the PA site of a CH<sub>3</sub>OH molecule is not sufficient to produce the considerable red-shift in the C–O stretching frequency we observe in the red component (between  $-17$  and  $-26$  cm<sup>-1</sup> relative to the free CH<sub>3</sub>OH). So what is the origin of the red component?



**Fig. 12** The ratio of the pure CH<sub>3</sub>OH components (blue and middle) to the red component (seen only in mixtures with H<sub>2</sub>O) as a function of CH<sub>3</sub>OH/H<sub>2</sub>O ratio, R. The graph shows a linear relationship below R=0.5, with a gradient of  $3.2 \pm 0.1$ , and above R=1, with a gradient of  $10.2 \pm 0.5$ . The linear relationship confirms that the red component of the C–O stretch of CH<sub>3</sub>OH is directly related to the presence of H<sub>2</sub>O

It is clear that the red component of the C–O stretch band of methanol is indicative of the presence of H<sub>2</sub>O as it is only seen in the spectra when H<sub>2</sub>O is present in the matrix. Therefore, in order to distinguish the behaviour of this 'water' component and its relationship with the 'methanol' components, we have plotted the sum of the blue and middle components (the only components present in pure CH<sub>3</sub>OH) as a ratio of the red component (present exclusively in the presence of H<sub>2</sub>O) against CH<sub>3</sub>OH/H<sub>2</sub>O mixing ratio, as shown in Figure 12. The graph shows a linear relationship below R=0.5, with a gradient of  $3.2 \pm 0.1$ , and above R=1, with a gradient of  $10.2 \pm 0.5$ . Indeed, the linear relationship confirms that the red component of the C–O stretch of CH<sub>3</sub>OH is directly related to the presence of H<sub>2</sub>O. Stoichiometrically, the turning point occurs over a range of R, going from an environment where there are two H<sub>2</sub>O molecules to every CH<sub>3</sub>OH (R=0.5) to an environment where there is one H<sub>2</sub>O to every CH<sub>3</sub>OH (R=1). This suggests that the red component is related to the hydrogen bonded molecular coordination number.

In crystalline H<sub>2</sub>O, molecules are able to arrange in tetrahedral structures, forming hydrogen bonds with four nearest neighbours - two PA bonds at the two lone pairs of electrons on the oxygen atom and two PD bonds with the O–H groups. In contrast, in pure crystalline CH<sub>3</sub>OH the molecules arrange in linear chains as each CH<sub>3</sub>OH molecule forms hydrogen bonds with just two nearest neighbours - a PA bond with only one lone pair of electrons on the oxygen atom and one PD bond with the O–H group. In an amorphous solid, however, there is no long-range order that is not too dissimilar to that of the liquid phase. In the less ordered structure in liquid CH<sub>3</sub>OH, the molecules arrange in chains, with bi-coordinated hydrogen bonds being the most probable, and the less probable single and tri-coordinated hydrogen bonds forming terminated chains and branches respectively. Thus in a mixture of CH<sub>3</sub>OH and H<sub>2</sub>O, we would expect a mixture of different hydrogen bond coordination numbers ranging from 1 to 3. In fact, computational studies have shown that the mean dipole moment of the CH<sub>3</sub>OH molecule depends on the number of hydrogen bonds the molecule makes with its nearest neighbours and that the dipole moment increases with increasing number of hydrogen bonds, suggesting substantial rearrangement of the molecular electron density<sup>38</sup>. The authors point out that the observed trend in liquid CH<sub>3</sub>OH closely resembles that of liquid H<sub>2</sub>O. Hence the correlation between H<sub>2</sub>O concentration with the relative area of the 'red' component below R=0.5, together with the large red-shift in frequency in the C–O stretch, that is associated with a PA hydrogen bond, would seem to suggest that CH<sub>3</sub>OH molecules are forming more than one PA bond with the H<sub>2</sub>O molecules - similar to the two PA bonds that H<sub>2</sub>O molecules make with the two lone pairs of electrons on the oxygen atom.

An experimental and computational study carried out on the adsorption of a single CH<sub>3</sub>OH molecule on H<sub>2</sub>O clusters<sup>58</sup> has shown that a CH<sub>3</sub>OH molecule binds to the H<sub>2</sub>O cluster and simultaneously acts as a PA and a PD (as would be expected of most molecules in the bulk of a solid) in a cyclic structure. A particularly interesting result of their experiment is that the CH<sub>3</sub>OH molecule forms a *third* hydrogen bond with another H<sub>2</sub>O, using the second lone pairs of electrons on the oxygen atom. The CH<sub>3</sub>OH molecule thus simultaneously acts as a PA to two H<sub>2</sub>O molecules. Buck *et al.* report that empirical calculations show that this additional interaction causes a further red-shift in the C–O stretching frequency corroborates our hypothesis about the origin of the red component in our data: a CH<sub>3</sub>OH molecule acting as a double PA to two PD H<sub>2</sub>O molecules. Referring back to Figure 12, the gradual change in gradient in the graph occurs between R=1 and R=0.5 a region from where there is one H<sub>2</sub>O to every CH<sub>3</sub>OH to where there are two H<sub>2</sub>O molecules to every CH<sub>3</sub>OH. The constant gradient below R=0.5 (more than two H<sub>2</sub>O molecules per CH<sub>3</sub>OH molecule), is where the most probable arrangement is one where each CH<sub>3</sub>OH acts as a double PA to two H<sub>2</sub>O molecules. The constant gradient above R=1 (less than one H<sub>2</sub>O molecule per CH<sub>3</sub>OH), is where the most probable arrangement is one where CH<sub>3</sub>OH acts as a PA to either one H<sub>2</sub>O or a CH<sub>3</sub>OH molecule. From Figure 10 it can be seen that the middle component reaches saturation around R=2, where there are two CH<sub>3</sub>OH molecules to every H<sub>2</sub>O molecule.

### 3.4.3 Bringing evidence together from the O–H, C–H and C–O stretch regions.

The sub-components in the C–O stretch band of CH<sub>3</sub>OH clearly indicate that there is preferential bonding between CH<sub>3</sub>OH and H<sub>2</sub>O, and that CH<sub>3</sub>OH(PA)⋯H<sub>2</sub>O(PD) is the preferred arrangement, even in vapour deposited samples at 30 K. Furthermore, the mixing between the two species in the amorphous solid appears to be inhomogeneous. This is evidenced by the presence of the red component even at high R. For example in mixtures above R=1, where there is less than one H<sub>2</sub>O molecule for every CH<sub>3</sub>OH molecule, the presence of the red component indicates that for some CH<sub>3</sub>OH molecules there are 2H<sub>2</sub>O molecules hydrogen bonded to them in a CH<sub>3</sub>OH(2PA)⋯2H<sub>2</sub>O(PD) arrangement that gives rise to the red component in the C–O stretch profile. In fact this behaviour is similar to that of liquid mixtures where evidence of clustering and inhomogeneity have been reported<sup>59–61</sup>. Monte Carlo simulations of CH<sub>3</sub>OH/H<sub>2</sub>O mixtures have shown two distinct regimes in the behaviour of the hydrogen bonded network that are related to a change from a percolating regime (below R=1) to a non-percolating regime<sup>60</sup>. It is interesting to note that in our case this is linked to the bonding preference between the molecules as they adsorb during sample growth, as they are unlikely to rearrange at 30 K, unlike the dynamic structure of hydrogen bonded liquids. This is consistently evident in the global structure of the amorphous solid via the profiles of the C–O, C–H and the O–H stretch modes as a function of R.

It has been reported that a red-shift in the C–O stretching frequency is also expected during the formation of a hydrogen bond with a methyl group due to intramolecular charge redistribution<sup>55</sup>. The weak hydrogen bond formed between one of the hydrogen atoms in the methyl group of CH<sub>3</sub>OH and a lone pair of electrons on a neighbouring H<sub>2</sub>O molecule is accompanied by a weak *intermolecular* orbital interaction between the proton accepting lone pair and a C–H ( $\sigma^*$ ) antibonding orbital. This is thought to result in an increase in the occupancy of the C–O  $\sigma^*$  antibonding orbital corresponding to weakening and elongation of the C–O bond and hence an observed red-shift in the C–O stretching frequency. Consequently there is an *intramolecular* charge transfer whereby a decrease in the in the orbital interaction between the lone pairs of electrons on the CH<sub>3</sub>OH oxygen atom and the C–H  $\sigma^*$  antibonding orbital occurs, which may explain the strengthening and shortening of the C–H bond and hence the observed blue-shift in the asymmetric C–H stretching frequency. Turning this around, Keefe and Istvanikova<sup>55</sup> suggest that the blue-shifts in C–H stretching modes could also be due to CH<sub>3</sub>OH acting as a PA via a lone pair of electrons on the oxygen atom. In this case there is also a decrease in the *intramolecular* orbital interaction between the oxygen lone pair and the C–H  $\sigma^*$  antibonding orbital as the occupancy in the CH<sub>3</sub>OH lone pair decreases during PA hydrogen bond formation. This results in a subsequent decrease in the occupancy of the C–H  $\sigma^*$  antibonding orbital and hence a strengthening, shortening and corresponding blue-shift in the C–H stretching frequency. So how would 2PA bonds on the O atom affect the C–H stretch region? In either case, in our experiments we observe both a blue-shift in the C–H

stretching modes and the presence of the red-shifted red component in the C–O stretch mode, both consistent with each other. It is interesting to note that the onset of blue-shifting in the C–H stretching frequency in Figure 6 is concurrent with the change in the slope in Figure 12 and also with the change in the slope of the O–H band position in Figure 4, all around R=0.6–0.75. Furthermore, a new band that appears and grows in intensity below R=0.6 in the C–H stretching region (Figures 5 and 6) may also be related to the red C–O stretch component. With the C–O bond linking the CH<sub>3</sub> and the OH ends of the CH<sub>3</sub>OH molecule there is clearly a cooperative effect between *intermolecular* interactions via the CH<sub>3</sub> hydrogens, the double PA oxygen lone pairs and PD O–H hydrogen resulting in significant *intramolecular* charge redistribution. These effects are concurrent across the different regions of the spectrum with a clear change in the bonding regime occurring below R=0.6–0.7. At high H<sub>2</sub>O concentrations such as bonding conformations must therefore become sterically favourable within the amorphous solid.

## 4 Conclusions

We have carried out a detailed systematic study of the infrared spectroscopy of mixtures of CH<sub>3</sub>OH and H<sub>2</sub>O at 30 K as a function of concentration. It is clear that CH<sub>3</sub>OH and H<sub>2</sub>O interact strongly within the solid matrix and that the nature of their interaction is strongly dependent on the CH<sub>3</sub>OH/H<sub>2</sub>O mixing ratio, R. Evidence from the O–H and C–H stretch band positions and detailed analysis of the sub-components of the C–O stretch band clearly indicate that there is a dramatic change in molecular coordination in the mixed hydrogen bonding network with two distinct regimes evident below and above R=0.6–0.7.

Detailed analysis of the C–O stretch band reveals that it consists of three sub-components in the mixed samples, with a 'red' component that is only present with H<sub>2</sub>O. The origin of the 'blue' and the 'middle' components are assigned to environments within the ice matrix in which dominant interactions involve CH<sub>3</sub>OH hydroxyl groups as proton donors and acceptors respectively. The 'red' component has been assigned to the CH<sub>3</sub>OH molecules in an environment where the molecules can act as double proton acceptors to two H<sub>2</sub>O molecules via both the lone pairs of electrons on the oxygen atom. The presence of the 'red' component at greater R might also suggest inhomogeneity in the mixing between CH<sub>3</sub>OH and H<sub>2</sub>O. There is evidence that there is preferential hydrogen bonding of the CH<sub>3</sub>OH molecule as a proton acceptor to proton donating H<sub>2</sub>O molecules as confirmed by direct correlation between the 'middle' and the 'red' components in the C–O stretch as a function of mixing ratio and a constant blue PD component.

Blueshifts in the C–H stretch positions were observed at mixing ratios below R=0.6–0.7 suggesting that the methyl group also participates in hydrogen bonding at low CH<sub>3</sub>OH concentrations. This is the ratio where we also observe a change in the hydrogen bonding behaviour, with the formation of higher coordinated bonds. It is thus expected that in the regime below R=0.6–0.7 the solid consists of more branched and cyclic structures with both the O–H and the CH<sub>3</sub> groups in CH<sub>3</sub>OH participating in hydrogen bonding, whereas more chains are expected above R=0.7

and that the solid amorphous mixture resembles the structure of liquid mixtures.

Our results demonstrate that not only does the C–O stretch of CH<sub>3</sub>OH provide us with insight into the hydrogen bonding nature and the structure of CH<sub>3</sub>OH/H<sub>2</sub>O condensed mixtures at 30 K, as a function of mixing ratio, but that it can also be used for the interpretation of observational spectra. The high sensitivity of the C–O stretch band profile on the CH<sub>3</sub>OH···H<sub>2</sub>O hydrogen bonding environment makes it an ideal candidate to infer spectroscopically whether CH<sub>3</sub>OH and H<sub>2</sub>O ices exist in segregated or mixed environments in the interstellar medium and on planetary bodies. Furthermore, the three clearly defined components in condensed ices may allow observational astronomers, through the inspection of this band, to determine the degree of mixing, and thus constrain the CH<sub>3</sub>OH/H<sub>2</sub>O component whilst simultaneously fitting other regions of the spectrum<sup>27</sup>. Though there is still considerable work required to fully understand the nature of interactions that gives rise to the C–O stretch components, for example as a function deposition temperature, deposition rate and film thickness as well as the effects of thermal and energetic processing, such work would also aid in the interpretation of the physical and chemical environment in which H<sub>2</sub>O and CH<sub>3</sub>OH ices are formed and exist in interstellar and planetary environments.

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