Ion irradiation effects on frozen methanol (CH$_3$OH)

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Abstract. We present some experimental results on the chemical-physical effects induced by ion irradiation on frozen methanol (CH$_3$OH), pure and mixed with water (H$_2$O). We have studied, by "in situ" infrared (IR) spectroscopy, samples of solid CH$_3$OH and H$_2$O:CH$_3$OH mixtures before and after irradiation, with 3-30 keV ions, at low pressures and low temperature (10 K). We have derived the integrated absorbance values of the main methanol bands. Furthermore we have analyzed the effects produced upon warm-up comparing the spectra of the irradiated H$_2$O:CH$_3$OH mixtures with the unirradiated ones at different temperatures. We found that after ion irradiation of methanol new species (such as H$_2$O, CO$_2$, CO, H$_2$CO and/or (CH$_3$)$_2$OH, CH$_4$) are formed, the profile (shape, width and peak position) of methanol bands changes and estimation of methanol abundance from different bands, in the same spectrum, gives different values. In particular, the CH$_3$OH/H$_2$O ratio estimated in an irradiated sample, from the 1460 cm^{-1} and 2830 cm^{-1} bands differs up to a factor 3-4. This study can have relevant astrophysical implications in fact, methanol has been detected as a component of icy grain mantles, from IR spectra of several protostellar sources. However the results concerning solid methanol abundance in the interstellar medium are quite controversial. In this work we focus our attention on the profile, in laboratory spectra, of the three methanol bands (at 1034, 1460, 2830 cm^{-1}) used to compute its abundance in icy grain mantles.

Key words: methods: laboratory – infrared: ISM: lines and bands – ISM: abundances – ISM: molecules

1. Introduction

It is well known that interstellar dust particles, inside dense molecular clouds (T $\simeq$ 10–20 K), are covered by icy mantles. These mantles are formed by accretion and/or reaction of gas phase species onto preexisting refractory grain cores. Moreover, during their lifetimes, icy grain mantles can interact with UV radiation and low energy cosmic rays.

Laboratory studies show that, as a consequence of energetic UV ($\lambda \leq 2000$ Å) and ion irradiation of icy samples, both

volatile and more complex species are produced and even a material with refractory properties may form (Greenberg 1982; Strazzulla & Johnson 1991). This latter could be still present in the diffuse interstellar medium.

Among other simple molecules, such as H$_2$O and CO, methanol (CH$_3$OH), a simple alcohol, has been detected as a component of icy grain mantles. In fact, different absorption features, assigned to solid methanol after comparison with laboratory spectra, have been identified along several lines of sight of obscured IR sources. The CH stretching mode at 3.54 μm (2830 cm^{-1}; Tielens 1989; Grim et al. 1991; Allamandola et al. 1992; Schutte et al. 1996a); the CH deformation and OH bending modes at 6.85 μm (1460 cm^{-1}; Tielens et al. 1984; Tielens & Allamandola 1987; Tielens 1989; Schutte et al. 1996b); the CH$_3$ rocking and the C–O stretching modes at 8.9 μm (1123 cm^{-1}) and 9.8 μm (1020 cm^{-1}) respectively (Schutte et al. 1991; Skinner et al. 1992).

One of the problems about methanol in the interstellar medium (ISM) is its abundance. Initially according to the observations in the 6 μm region it was estimated an abundance of about 50–80% with respect to water (Tielens & Allamandola 1987). After further observations in the 3 μm and 10 μm regions methanol abundance was constrained to only 4–17% (Grim et al. 1991; Allamandola et al. 1992; Schutte et al. 1991; Skinner et al. 1992; Chiar et al. 1996).

In order to explain this discrepancy on solid methanol abundance along the same line of sight, which depends on the band used to estimate it, other species have been searched to contribute to the 6.85 μm band. Among these, Grim et al. (1989) have suggested NH$_4^+$, an ion produced upon UV irradiation of frozen targets containing NH$_3$. But this ion band shows, in laboratory, changes in its profile when the sample is warmed-up. These changes with the temperature could not be reconciled with the profile of the 6.85 μm observed in a large number of sources with different conditions of temperature.

Alternatively, Pendleton et al. (1990) suggested that the discrepancy in the methanol abundance, obtained from different bands observed towards W33A, could be explained assuming that there is a reflection nebula associated with the disk geometry around the protostar. Thus the photon pathlength through the nebula may be different at different wavelengths: near-IR photons prefer to escape through the pole, the mid-IR photons,

instead, through the disk. Then, longer wavelength bands could be more intense relative to shorter wavelength ones. In this view, the spectral features in the 6 μm region should give the right CH$_3$OH/H$_2$O ratio. However after observations in the 10 μm region, which give 4–17% of methanol with respect to water, this suggestion is no longer satisfactory.

Recently high resolution, high signal to noise SWS (ISO) spectra in the 5.3–8.3 μm region towards NGC 7538 IRS9 have been obtained (Schutte et al. 1996b) and a number of candidates for the 6.8 μm band are reviewed. On the basis of the methanol abundance estimated along the same line of sight from the C–H stretch band (Allamandola et al. 1992), Schutte et al. (1996b) conclude that methanol contributes to the 6.8 μm band at the 25% level and that most of the band has to be carried by another species. However none of the species examined appears to satisfy the observational constraints.

Another open question about solid methanol in the ISM is its formation. Three formation mechanisms have been taken into account (UV irradiation, grain surface reactions and condensation from the gas phase) which give an amount ($\simeq$2% with respect to water) of methanol being too low with respect to that estimated from the interstellar spectra (see Grim et al. 1991).

For the above issues, "methanol in ISM" is an interesting subject for the astrophysical research. Many laboratory spectra of pure methanol, and mixtures with astrophysically relevant species, have been studied and compared to observed spectra (Tielens & Allamandola 1987; Grim et al. 1991; Schutte et al. 1991; Allamandola et al. 1988, 1992; Sandford & Allamandola 1993).

The effects induced upon UV irradiation on H$_2$O:CH$_3$OH mixtures and pure CH$_3$OH have been studied by Allamandola et al. (1988) and Gerakines et al. (1996).

Results on ion irradiation experiments on methanol targets have already been presented by Baratta et al. (1994), Hudson & Moore (1995), Strazzulla et al. (1995) and Moore et al. (1996). These papers present results on the spectral identification of new species synthesized after ion irradiation of CH$_3$OH and H$_2$O:CH$_3$OH ices. Moore et al. (1996) also give, by mass spectroscopy, information on the volatile species released during slow warming of the samples.

In this paper we present a new detailed study of the effects induced by ion irradiation of frozen methanol, pure and mixed with water. In particular we have studied the profile (shape, width and peak position) of methanol bands and the formation of new species. The technique used for the analysis is "in situ" infrared spectroscopy. In Sect. 2 we discuss the experimental apparatus and the calibration procedure. In Sect. 3 we present our laboratory results. We report some astrophysical implications of the laboratory data in Sect. 4.

2. Experimental apparatus

The experimental apparatus used has been already described elsewhere (Strazzulla & Baratta 1991; Baratta & Palumbo 1998).

Table 1. Spectroscopic properties of solid methanol

Vibration mode	$\tilde{\nu}$ (cm^{-1})	λ (μm)	A (10^{-17} cm/mol)
O–H stretch	3260	3.07	11.2
C–H stretch (asym)	2961	3.38	1.1
C–H stretch (sym)	2830	3.53	0.47
C–H def & O–H bend	1460	6.84	0.91
–CH$_3$ rock	1129	8.86	0.15
C–O stretch	1034	9.7	1.3
torsion	694	14.4	

A stainless steel vacuum chamber (P $<$ 10^{-7} mbar) is faced to a spectrophotometer (4400–400 cm^{-1} = 2.27–25 μm) through KBr windows. At the centre of the chamber there is a cold finger, placed in thermal contact with the tail section of a closed-cycle helium cryostat (10–300 K). A silicon substrate (of about 500 μm) is put in contact with the cold finger.

The sample, a pure gas or a mixture, is prepared in a chamber and after admitted by a gas inlet, through a needle valve, into the vacuum chamber, where is accreted onto the silicon crystal. During and after accretion samples can be bombarded by 3–60 keV ions. The beam produces a 2 $\times$ 2 cm^2 spot on the target (greater than the spot of the IR beam) and current densities in the range of several 10^{-1} to a few μampere/cm^2 in order to avoid macroscopic heating of the sample. We express the amount of energy released to the sample (dose) in eV per small molecule (16amu), because it is a convenient way to characterize chemical changes (Strazzulla & Johnson 1991) and to have a comparison with other experiments with different samples. In addition the ion beam and the infrared source are mutually perpendicular while they form an angle of 45 degrees with the substrate plane, thus before, during and after irradiation, spectra can be obtained without tilting the sample.

For calibration purposes it is necessary to know the deposition rate (Å/sec) of a gas. It is possible to calibrate the thickness of a deposited ice, as a time function, by counting the interference fringes of a reflected laser light (He-Ne λ=6328 Å; Spinella et al. 1991). The laser beam is, in fact, partially reflected and transmitted by two interfaces (vacuum-sample and sample-substrate). Thus we have estimated the integrated absorbances (A in cm/molecule) of methanol bands from the knowledge of the thickness of the sample and the integrated optical depth of each band. Our results are reported in Table 1. All spectra, presented in the following sections, have been taken with a resolution of 2 cm^{-1}, and a sampling of 1 cm^{-1} and are ratioed to the background spectrum which includes the silicon substrate.

3. Ion irradiation effects: laboratory results

Methanol is a simple alcohol and its spectrum (see Fig. 1) at 10 K shows different absorption bands due to molecular vibrations. Peak position, vibration mode, and integrated absorbance A of the main methanol features are reported in Table 1.
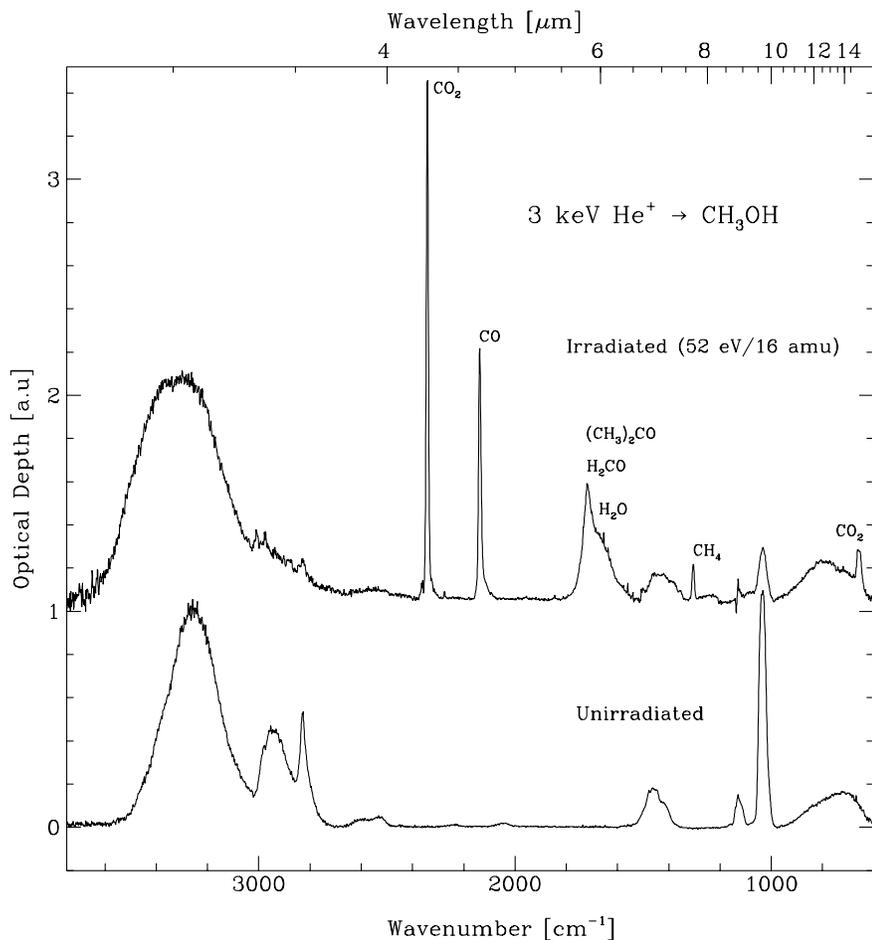
Fig. 1. IR spectra of pure methanol deposited on a cold (10 K) substrate before and after ion irradiation with 3 keV helium ions (52 eV/16amu). The spectra have been normalized to the O–H stretching band

Several experiments have been done at low temperatures (10 K) and low pressures ($\leq 10^{-7}$ mbar), in order to analyze, by infrared spectroscopy, the physical-chemical effects induced by ion irradiation of frozen methanol, pure and mixed with water. We have studied the formation of new species (Sect. 3.1) and examined the profile (shape, width and peak position) of the different methanol absorption bands of the deposited gas, compared with that obtained after irradiation (Sects. 3.2, 3.3). We have also warmed-up our samples and made a comparison between irradiated and unirradiated spectra (Sect. 3.4).

3.1. Formation of new species

In Fig. 1 we compare the IR spectrum of pure methanol frozen at 10 K with that obtained after irradiation with 3 keV helium ions at a dose of 52 eV/16amu. New bands (labeled in figure) appear in the irradiated sample at about 660 and 2344 (CO$_2$), 1305 and 3010 (CH$_4$), 1655 (H$_2$O), 1720 (H$_2$CO and/or (CH$_3$)$_2$CO), 2136 (CO) cm^{-1}.

3.1.1. H$_2$O

Among the newly formed species we identify H$_2$O. This identification is based on the observation of the band at 1655 cm^{-1}, that we associate to the peculiar H–O–H bending mode of

water molecules, and on the strongly modified profile of the 3260 cm^{-1} band due to the O–H stretching mode.

In Fig. 2 we show a comparison, in the 3700–2600 cm^{-1} region, between the spectra of unirradiated H$_2$O:CH$_3$OH (x:1) mixtures (solid lines) and that of pure methanol ice, after irradiation with a dose of about 30 eV/16amu (dotted lines). The figure shows that the profile of the 3 μm band depends on the H$_2$O/CH$_3$OH ratio. As the amount of water increases the band width increases and the peak position shifts to higher wavenumbers.

The lowest panel show that after ion irradiation of pure methanol the band is broader and shifts to longer wavenumbers with respect to that of the unirradiated sample. It is evident that the former well compare to the profile of the 1:1 mixture, while the bands of the 2:1 and 10:1 mixtures are slightly broader. This support the conclusion that water is produced after ion irradiation of methanol. The formation of water is also evidenced from the relative ratio between the intensity of the 9.7 μm and the 3 μm bands of methanol which decreases after ion irradiation. We exclude the possibility that the presence of water is due to spurious condensation during the experiment. In fact the amount of water observed is more than one order of magnitude larger than the amount of calibrated spurious water (≤ 1 Å/min).

Fig. 3 shows the estimated CH$_3$OH/H$_2$O ratio as a function of irradiation dose and initial mixture. The abundance of
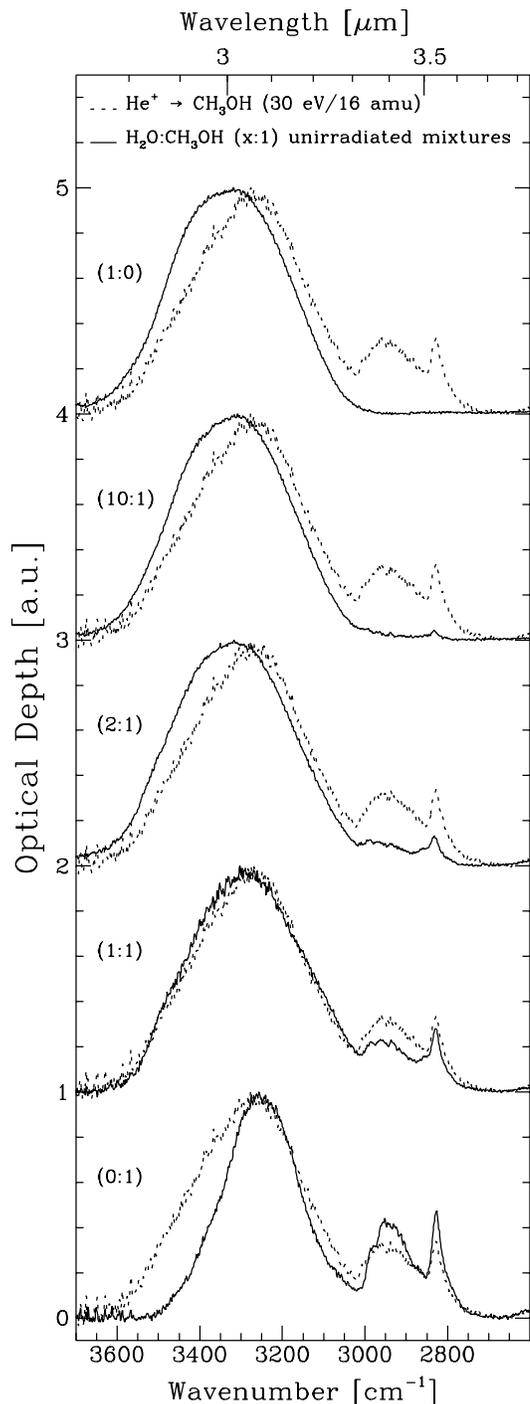
Fig. 2. The IR spectra of unirradiated H$_2$O:CH$_3$OH (x:1) mixtures are compared with the spectrum of pure methanol irradiated with 3 keV helium ions (30 eV/16amu). All the spectra have been normalized to the O–H stretching band
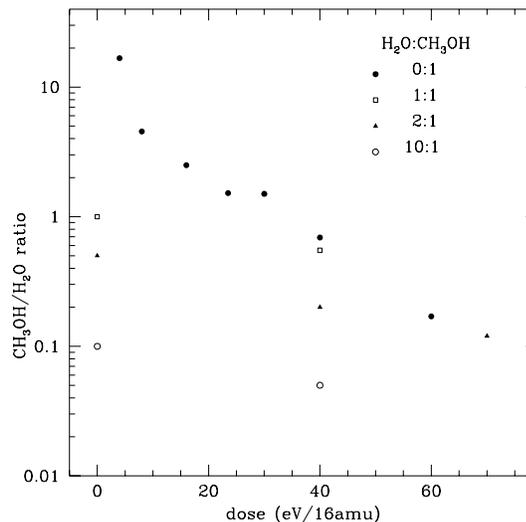

Fig. 3. CH$_3$OH/H$_2$O ratio as a function of irradiation dose and initial mixture.

(solid lines) with those of the same mixtures irradiated with 3 keV helium ions (about 40 eV/16amu; dotted lines). This figure shows that the band of pure irradiated methanol is different from the unirradited one, while in the 2:1 and 10:1 mixtures this difference is hardly detectable. This implies that the main discriminating process is the formation of water. But if the starting mixture is 10:1, the water produced after irradiation is negligible. Finally, in the right panel of Fig. 4, we compare IR spectra, in the 3700–2600 cm^{-1} region, of the unirradiated H$_2$O:CH$_3$OH (x:1) mixtures (solid lines) with that of pure water (dotted lines). This shows that only in a 1:1 mixture the profile of the O-H stretching mode is clearly affected by the presence of methanol.

3.1.2. Other species

Another spectral region analyzed in this work is beetwen 1900 and 1200 cm^{-1}. A new feature, at 1719 cm^{-1}, superimposed to the 1655 cm^{-1}, is also evident in Fig. 1.

Moore et al. (1996) have observed, in their spectrum of a H$_2$O:CH$_3$OH (1.6:1) mixture irradiated with protons, the 1720 cm^{-1} band and two new features at 1249 and 1500 cm^{-1} that they have associated to the characteristic formaldehyde (H$_2$CO) vibration modes. They have, also, estimated the abundance of formaldehyde and inferred that the H$_2$CO contribution to the band at 1720 cm^{-1} is 25%. Baratta et al. (1994) have pointed out that this band could be attributed to more than one species, such as acetone ((CH$_3$)$_2$CO) and formaldehyde (H$_2$CO), and it can not be used to estimate the abundance of any species.

Other species formed after ion irradaition are CO, CO$_2$, CH$_4$ identified from the band at about 2136 cm^{-1}, 2340 and 660 cm^{-1} and 3010 and 1303 cm^{-1} respectively. A detailed study of these bands has already been presented elsewhere and will not be reported here (see Palumbo 1997; Palumbo et al. 1998; Mulas et al. 1998).
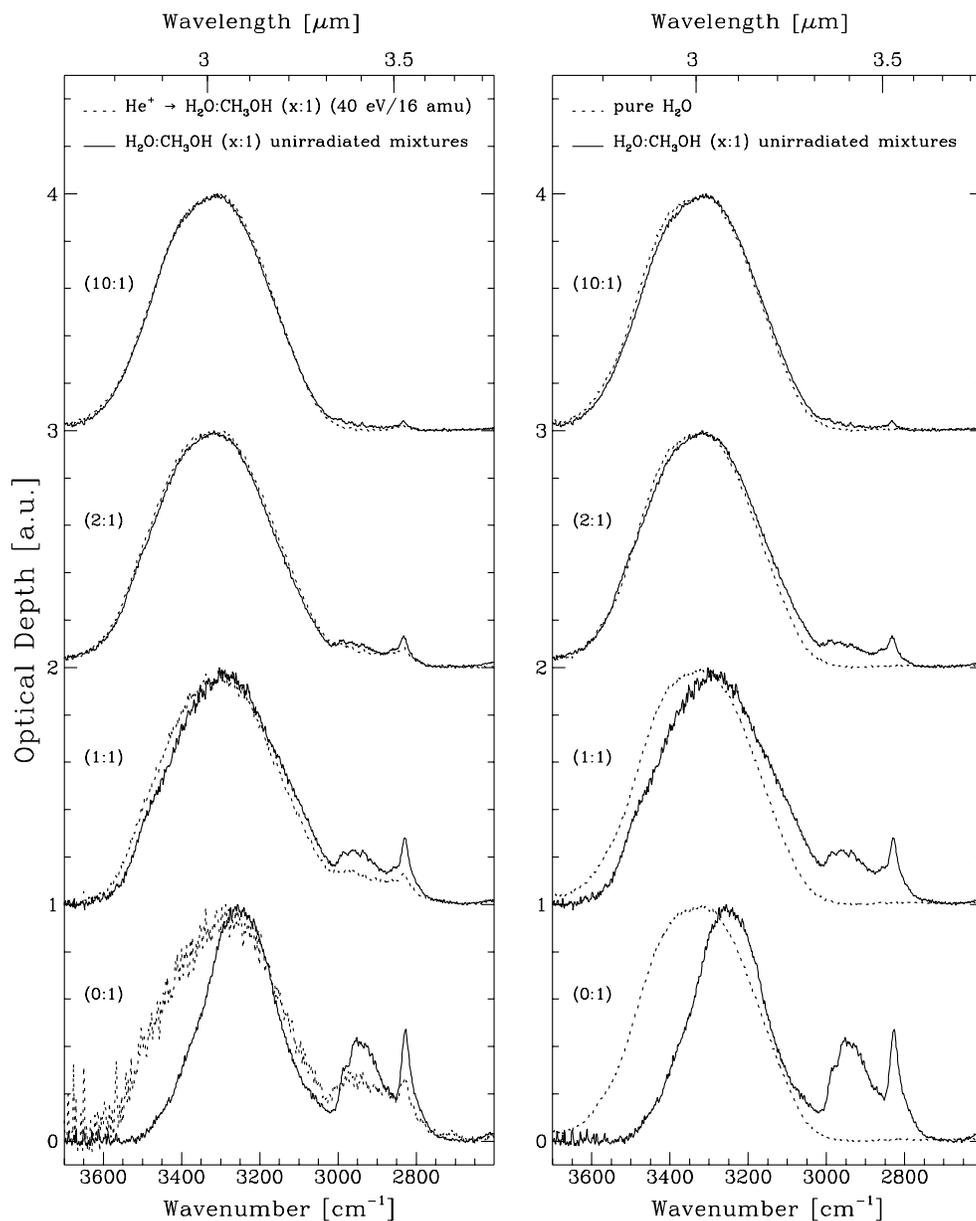
water has been estimated from the 1655 cm^{-1} band using $A= 1\times10^{-17}$ cm/molecule (Hudgins et al. 1993) while the abundance of methanol using the 1034 cm^{-1} band and the A value reported in Table 1.

In Fig. 4 we compare (left panel) the IR spectra, in the 3700–2600 cm^{-1} region, of unirradiated H$_2$O:CH$_3$OH (x:1) mixtures

Fig. 4. IR spectra, in the 3700 to 2600 cm^{-1}, of unirradiated H$_2$O:CH$_3$OH (x:1) mixtures (*solid lines*) are compared with those of the same mixtures irradiated with 3 keV helium ions (about 40 eV/16amu) (*dotted lines*) *left panel* and with that of a pure water (*dotted lines*) *right panel*. All the spectra have been normalized to the O–H stretching band

3.2. Modification of methanol bands

In this section we focus our attention to three methanol bands namely the C–O stretching mode (at about 1034 cm^{-1}), the CH deformation and OH bending modes (at about 1460 cm^{-1}) and the symmetric CH stretching mode (at about 2830 cm^{-1}). These features have been used to estimate the methanol abundance (mol/cm^2) in interstellar icy mantles.

The C–O stretching mode is often used to estimate the methanol abundance from laboratory spectra, because it is not superimposed to the bands of other species.

A comparison of the profile of the C–O stretching band in irradiated and unirradiated spectra of pure methanol and H$_2$O:CH$_3$OH mixtures is reported in Fig. 5. All plotted spectra are normalized to the maximum and the dotted line gives the peak position in the pure methanol sample. Analyzing the

unirradiated bands (left panel) we observe that, as the amount of water increases in the mixture, the band profile changes: its peak position is shifted to lower wavenumbers (from 1034 cm^{-1} to 1020 cm^{-1}) and its profile is asymmetric. This shift is likely due to methanol molecules embedded in a water matrix.

In H$_2$O:CH$_3$OH unirradiated mixtures the band becomes slightly narrower, its full width half maximum (FWHM) varies from 35 cm^{-1} to 27 cm^{-1}, as the amount of water increases. In pure methanol we observe a FWHM equal to 29 cm^{-1}.

After ion irradiation, as shown in Fig. 5 (right panel), the C–O stretching profile is modified. Peak position shifts to lower wavenumbers and this is typical for methanol embedded in water; while FWHM does not change. In the 10:1 irradiated mixture a shoulder at about 1034 cm^{-1} appears.

The methanol band at about 1460 cm^{-1} is due to both the CH deformation and the OH bending modes (see Fig. 1). In
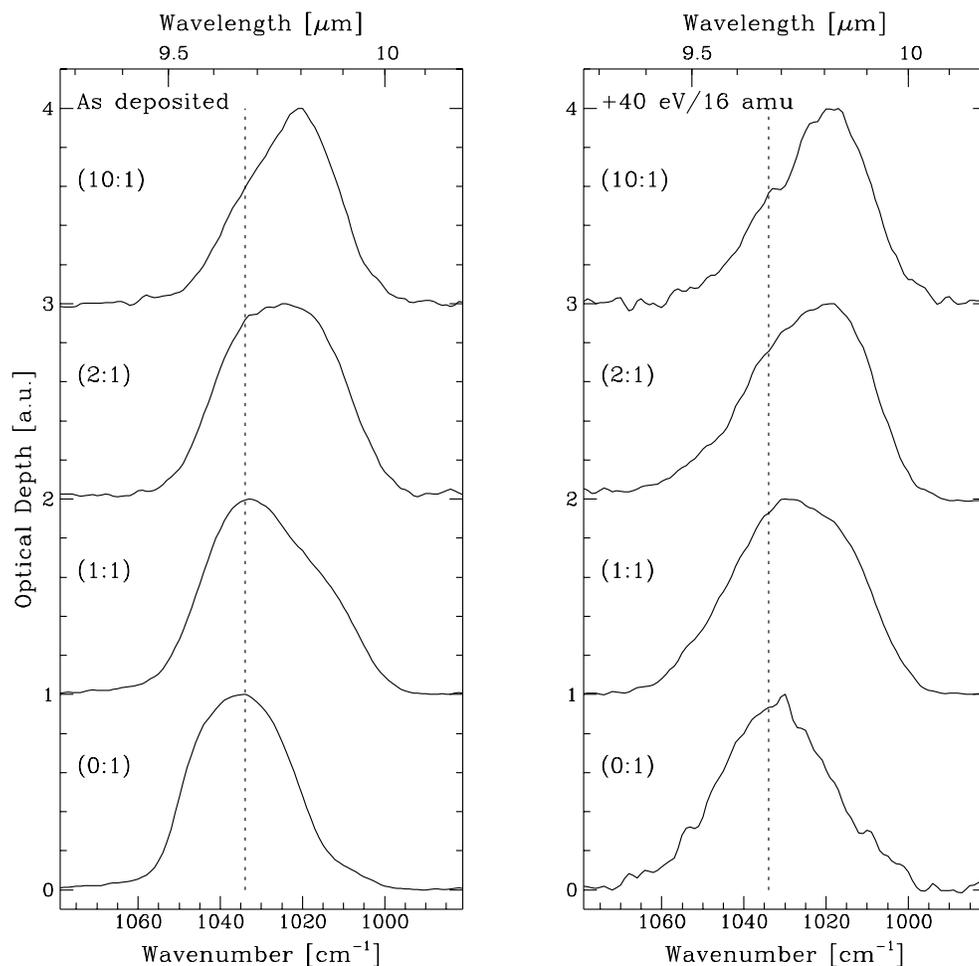
Fig. 5. The C–O stretching profile in unirradiated $H_2O:CH_3OH$ (x:1) mixtures [left panel] is compared with that in irradiated mixtures at 10 K *right panel*. A dotted line at $1034\,cm^{-1}$ has been drawn for reference

pure methanol this band shows three peaks at about 1480, 1463, $1450\,cm^{-1}$ equally intense and a shoulder at about $1430\,cm^{-1}$. The same structure is observed in the 1:1 and 2:1 mixtures, where the shoulder at $1430\,cm^{-1}$ becomes less intense. In the 10:1 mixture the peak at $1480\,cm^{-1}$ appears stronger than the others. As the amount of water increases, the band becomes narrower, its FWHM decreases from $86\,cm^{-1}$ in pure methanol to $68\,cm^{-1}$ in a 10:1 mixture.

The irradiated spectra show a strong modification of the analyzed region, as shown in Fig. 1. After ion irradiation the $1460\,cm^{-1}$ band becomes broader.

The CH stretching modes fall at about $2830\,cm^{-1}$ and $2950\,cm^{-1}$ (Fig. 4). In the unirradiated $H_2O:CH_3OH$ mixtures, as the amount of water increases, the asymmetric vibration at about $2951\,cm^{-1}$ becomes broader. The profile of the symmetric CH stretching band does not really change in the different mixtures as the amount of water increases: its peak position shows a slight shift from 2826 to $2832\,cm^{-1}$, while its FWHM decreases from 32 to $16\,cm^{-1}$. In the different mixtures the symmetric CH stretching band shows a shoulder at about $2850\,cm^{-1}$, that is not present in the spectrum of pure methanol.

After ion irradiation, we observe that the CH stretching bands are strongly destroyed (see Fig. 4). The $2830\,cm^{-1}$ band does not shift, its FWHM increases compared to that of the same

unirradiated sample. There is a shoulder at about $2900\,cm^{-1}$ due to the contribution of the $2951\,cm^{-1}$, that, upon bombardment, appears strongly modified (the band becomes flatter).

3.3. Methanol abundance estimation

Because of ion irradiation, methanol molecules are broken and in fact other species form as a consequence of recombination of produced radicals. Furthermore it is well known that the structure of the ice is modified after ion irradiation (Baratta et al. 1994).

We have found that the different bands are differently affected by ion irradiation and hence give different information on the amount of methanol in the irradiated mixture.

Hudgins et al. (1993) report that the integrated absorbance of methanol bands changes when it is mixed in with water. We have shown that in fact water is formed after irradiation of methanol. However we have estimated that the different amount of methanol deduced by the different bands cannot be ascribed to the change of the integrated absorbances.

In Fig. 6 we compare the amount of methanol as deduced from the $1460\,cm^{-1}$ and the $2830\,cm^{-1}$ bands to the amount deduced fron the $1034\,cm^{-1}$ band (N(1034) in mol/cm²) as a function of irradiation dose. The figure shows that the
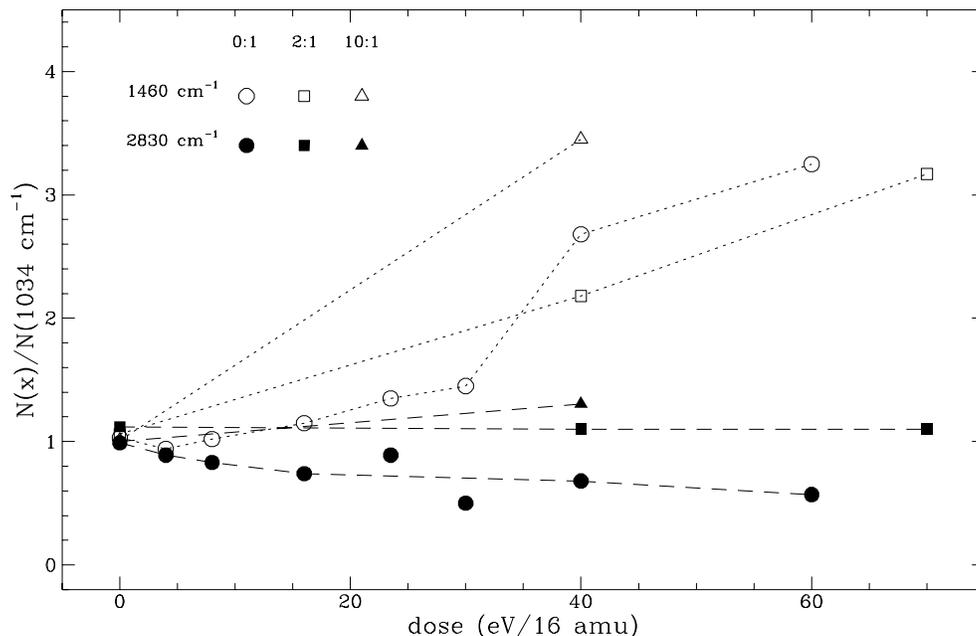
Fig. 6. Methanol abundance measured from the 1460 and 2830 cm^{-1} bands in the H$_2$O:CH$_3$OH mixtures ratioed to that obtained from the 1034 cm^{-1} at different suffered doses. Dotted and dashed lines have been drawn to guide the eye. Dotted lines connect data points relative to N(1460)/N(1034) while dashed lines connect data points relative to N(2830)/N(1034)

N(2830)/N(1034) ratio is almost constant and equal to $\sim$ 1, while the N(1460)/N(1034) ratio increases as a function of irradiation dose and of the initial mixture. Hence the amount of methanol deduced by the 1460 cm^{-1} band after ion irradiation is greater than that deduced from the 2830 and 1034 cm^{-1} bands.

Points at dose equal to zero should strictly be equal to 1. This is not the case because, as pointed out by Hudgins et al. (1993), the integrated absorbance of methanol bands depends on the H$_2$O/CH$_3$OH ratio. For these calculations we have used A values relative to pure methanol.

These results, presented here for the first time, could have important astrophysical implications as we will discuss in Sect. 4.

3.4. Warm-up effects

In Fig. 7 (left panel) we compare the profile of the C–O stretching band in pure methanol and in mixtures with water, as the temperature T increases from 10 to 150 K. In pure methanol the C–O stretching feature changes little upon warm-up, only its peak position shifts slightly to lower wavenumbers (1029 cm^{-1}) at 150 K, while its peak absorbance increases. In H$_2$O:CH$_3$OH mixtures two peaks, at 1033 cm^{-1} and 1016 cm^{-1}, appear whose relative intensity depends on the initial mixture and on temperature. The formation of a new peak at 1034 cm^{-1} has been already observed in laboratory spectra of H$_2$O:CH$_3$OH mixture (20:1), analyzed by Schutte et al. (1991). They suggest that this peak is due to methanol embedded in more annealed H$_2$O ice.

In Fig. 7 (right panel) we compare at different temperatures (T=10 – 100 – 150 – $\geq$160 K) the profile of the C–O stretching band in the H$_2$O:CH$_3$OH (x:1) mixtures after ion irradiation at 10 K. In pure methanol we observe the same trend of the unirradiated sample: peak absorbance increases as the temperature

goes up. This happens also in the 1:1 mixture. In H$_2$O:CH$_3$OH mixtures (2:1 and 10:1) again two peaks appear whose relative intensity, however, is affected by ion irradiation.

Another step of this section is to compare the effects produced, after warm-up, of irradiated and unirradiated H$_2$O:CH$_3$OH (x:1) mixtures in the whole spectral range (3900–600 cm^{-1}). The temperature range is 10–200 K.

All the spectra reported (Figs. 8–10) show a band at 1100 cm^{-1} upon warm-up. This band is due to the silicon substrate on which the gas is accreted. In fact, the profile of the silicon band changes as the temperature increases and is different from that obtained in the background spectrum at 10 K.

Previous results have been presented in Strazzulla et al. (1995), where a comparison between the spectra of an unirradiated H$_2$O:CH$_3$OH mixture (1:1) with those of the irradiated mixture at different temperatures is shown.

In Fig. 8 we analyzed the IR spectra of unirradiated and irradiated (52 eV/16amu) pure methanol at different temperatures (T = 10–200 K). All the spectra are normalized to the 3260 cm^{-1} band. Pure methanol sublimes at about 160 K. The spectrum at 150 K shows a deep modification of each methanol band. The CH deformation and OH bending modes show a profile with one peak more intense at 1474 cm^{-1} and two peaks less intense at 1457 and 1513 cm^{-1}. New bands appear at 1341 cm^{-1} and at 681 cm^{-1}; this latter is superimposed to the OH torsion mode. Hudgins et al. (1993) have shown a spectrum of pure methanol at 120 K in which these new features are also present. They, in addition, observe also a splitting of the O–H stretching band. In our spectrum at 150 K this band presents a shoulder at 2985 cm^{-1}. All these changes suggest that a phase transition has occured between 100 and 150 K.

In the spectrum of irradiated methanol at 200 K all methanol features are still present. Thus, the sample has gained refractory
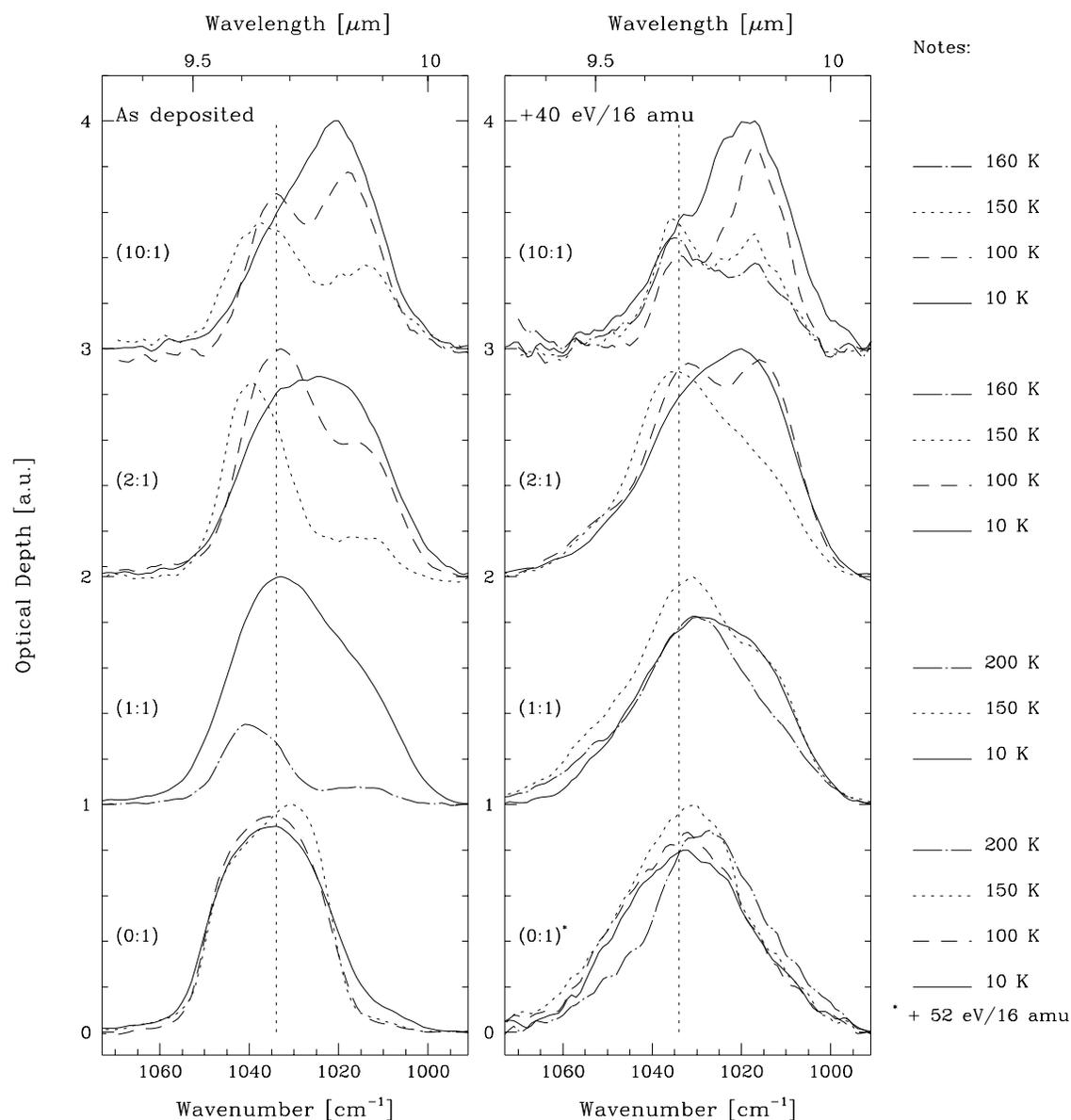
Fig. 7. C–O stretching band in a pure methanol spectrum and in H$_2$O:CH$_3$OH mixtures is compared with that observed after ion irradiation on the same samples at different temperatures (T= 10 – 100 – 150 – $\geq$ 160 K). A dotted line at 1034 cm^{-1} has been drawn for reference

properties. The profile of the 3260 cm^{-1} band suggests that no phase transition has occurred until 150 K.

The bands of the volatile species produced after ion irradiation, such as CO (2136 cm^{-1}) and CO$_2$ (2344 cm^{-1}), are still present at 150 K, far above their sublimation temperature. This means that, as a consequence of irradiation, these species have been trapped into the new refractory structure.

In addition the features at about 1680 cm^{-1} and 1719 cm^{-1} are still evident at 200 K, while the 2340 cm^{-1} is due to atmosferic CO$_2$, not perfectly purged.

Fig. 9 shows a comparison, at different temperatures (T = 10–180 K) between the spectra of an unirradiated H$_2$O:CH$_3$OH (2:1) mixture with those of the same mixture irradiated with a dose of 40 eV/16amu. In this case the deposited mixture sub-

limes at about 180 K. Methanol is still present at 150 K with an abundance of about 14% with respect to water. The profile of the 3260 cm^{-1} band becomes that of a crystal ice as the sample is warmed-up from 150 to 160 K.

At 160 K the irradiated spectrum shows that CO$_2$ (at about 2342 cm^{-1}), produced at 10 K, is still present, while the CO band (at about 2137 cm^{-1}) is present until 100 K. At 180 K the features at 1680 cm^{-1} and 1719 cm^{-1} are observed.

Finally, in Fig. 10 we compare the spectra of an unirradiated H$_2$O:CH$_3$OH (10:1) mixture with those of an irradiated mixture in the temperature range 10 to 180 K. In this case amorphous to crystal transition has already occurred at 160 K for the unirradiated sample and at this temperature the methanol abundance is estimated lower than 5% with respect to water. All the sam-
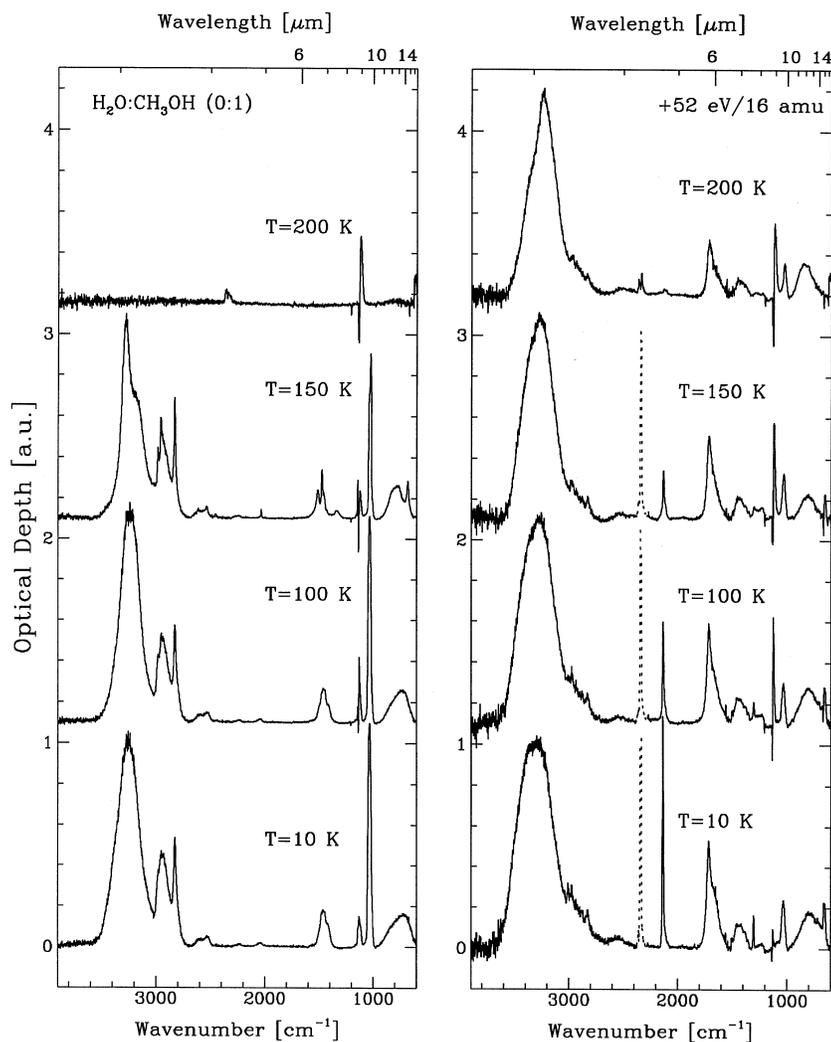
Fig. 8. IR spectra of unirradiated pure CH$_3$OH are compared, at different temperatures (T= 10 – 100 – 150 – 200 K), with those of methanol irradiated with 3 keV helium ions (52 eV/16amu). All the spectra are normalized to the 3260 cm^{-1} band. The profile of the CO$_2$ band at about 2340 cm^{-1}, because of its high peak intensity (about twice that of the 3260 cm^{-1} band), has been plotted, for clarity, up to optical depth equal to 1 (*dotted lines*)

ple sublimes at about 180 K. The methanol bands disappear at 170 K. The irradiated mixture show, instead, at 185 K a small feature at about 3200 cm^{-1}, that is going to decrease and disappear. This testifies that all the sample is going to sublime at that temperature. This sublimation temperature is lower than those of the other irradiated mixtures (250 K, 200 K, 190 K respectively for 0:1, 1:1, 2:1). This difference is due to the different percentage of refractory material produced after ion irradiation in different H$_2$O:CH$_3$OH mixtures.

In conclusion, we can say that, as a consequence of ion irradiation, methanol molecules are destroyed but different methanol bands give different information on the amount of methanol still present in the mixture; other species, not present in the unirradiated mixture, are formed; the irradiated samples show refractory properties and the produced volatile species are trapped into the new structure; phase transition occurs at higher temperature.

4. Discussion

Infrared absorption bands at about 2830, 1460, 1123 and 1020 cm^{-1} (3.54, 6.85, 8.9, 9.8 μm) have been observed along several lines of sight of obscured sources (e.g., Grim et al. 1991; Allamandola et al. 1992; Skinner et al. 1992; Schutte et al. 1996b). According to laboratory spectra these bands are attributed to solid CH$_3$OH in icy grain mantles.

However, the estimations of solid methanol abundance from the astronomical spectra are controversial. From the 2830 cm^{-1} (Grim et al. 1991, Allamandola et al. 1992) and the 1034 cm^{-1} bands (Schutte et al. 1991, Skinner et al. 1992) it has been deduced an amount of methanol $\sim$10% with respect to water. This is much smaller than that obtained from former low resolution spectra of the 1460 cm^{-1} band (Tielens & Allamandola 1987) which gives a value $\geq$ 50% with respect to water.

Recent high resolution ISO observations towards the embedded source NGC 7538 IRS9 have shown an absorption feature at about 1460 cm^{-1} (Schutte et al. 1996b). The authors consider the possibility that this feature is due to the C–H deformation mode of solid methanol. However, besides the goodness of the match between laboratory spectra and observations, they consider, on the basis of laboratory spectra, that the strength of the 1460 cm^{-1} band would require C–H and C–O stretching modes much stronger than observed. Then they conclude that methanol
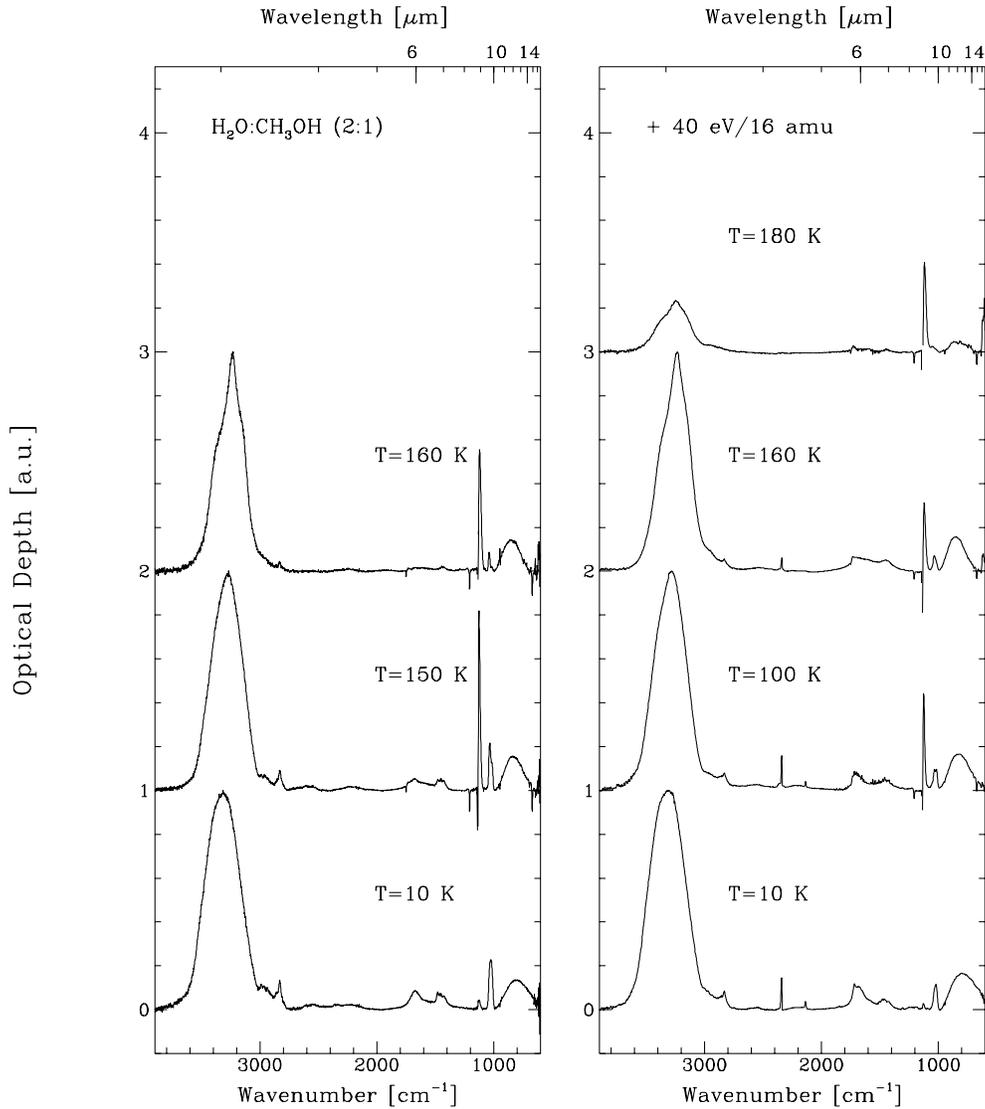
Fig. 9. IR spectra of an unirradiated $H_2O:CH_3OH$ (2:1) mixture are compared, at different temperatures (T = 10–180 K), with those of the irradiated mixture (40 eV/16amu). Spectra are normalized to the $3260\,cm^{-1}$ band

contributes to that band at the 25% level and most of it has to be carried by another species. However none of the species they have examined satisfy the observational constraints.

Skinner et al. (1992) have pointed out that the C–O stretch profile ($1034\,cm^{-1}$) is similar to that observed in laboratory spectra of $H_2O:CH_3OH$ mixtures, where the methanol concentration relative to water is ≥ 0.5, while the columnar abundances, computed from the observed bands, gives a lower CH_3OH/H_2O ratio (≤ 0.1). This discrepancy suggested that CH_3OH and H_2O are not well mixed along the line of sight of this protostar. In other words, Skinner et al. (1992) infer that solid methanol and water ice are located in independent grain components and these independent components may reflect chemical differentiation during grain mantle formation and/or partial outgassing close to the protostars. Such a differentiation of grain mantles along the same line of sight has also been inferred from the profile of the solid CO band (e.g., Tielens et al. 1991; Teixeira et al. 1998) and of the solid OCS band (Palumbo et al. 1995, 1997) towards a variety of objects. In particular, the profile of the OCS band

is well fitted by laboratory spectra relative to solid OCS in a methanol-rich matrix.

Experimental results, presented in this paper, have shown that ion bombardment produces relevant changes in the molecular structure of methanol. The flux of low energy cosmic rays irradiating grains in the interstellar medium is not well known. Jenniskens et al. (1993) gave a reasonable estimate of a proton (E = 1 MeV) flux ($J = 3\,cm^{-2} \cdot sec^{-1}$). The specific energy loss of 1 MeV protons in a typical grain containing heavy atoms (C, N, O, Si) is $S \simeq 5 \cdot 10^{-15}\,eV \cdot cm^2/atom$. Thus, after a time of $3 \cdot 10^{12} \leq t(sec) \leq 3 \cdot 10^{15}$, equal to icy grain mantles lifetime, the energy deposited on each grain (dose) is given by $S \cdot J \cdot t$ and values 0.05–50 eV/atom (C, N, O, Si) (Palumbo & Strazzulla 1993).

In this paper we have shown that the profile of methanol bands depends on the initial mixture and on irradiation and thermal history, that H_2O is formed after ion irradiation of methanol and that CH_3OH abundance estimation depends on the methanol band used. In particular after ion irradiation of a methanol-rich
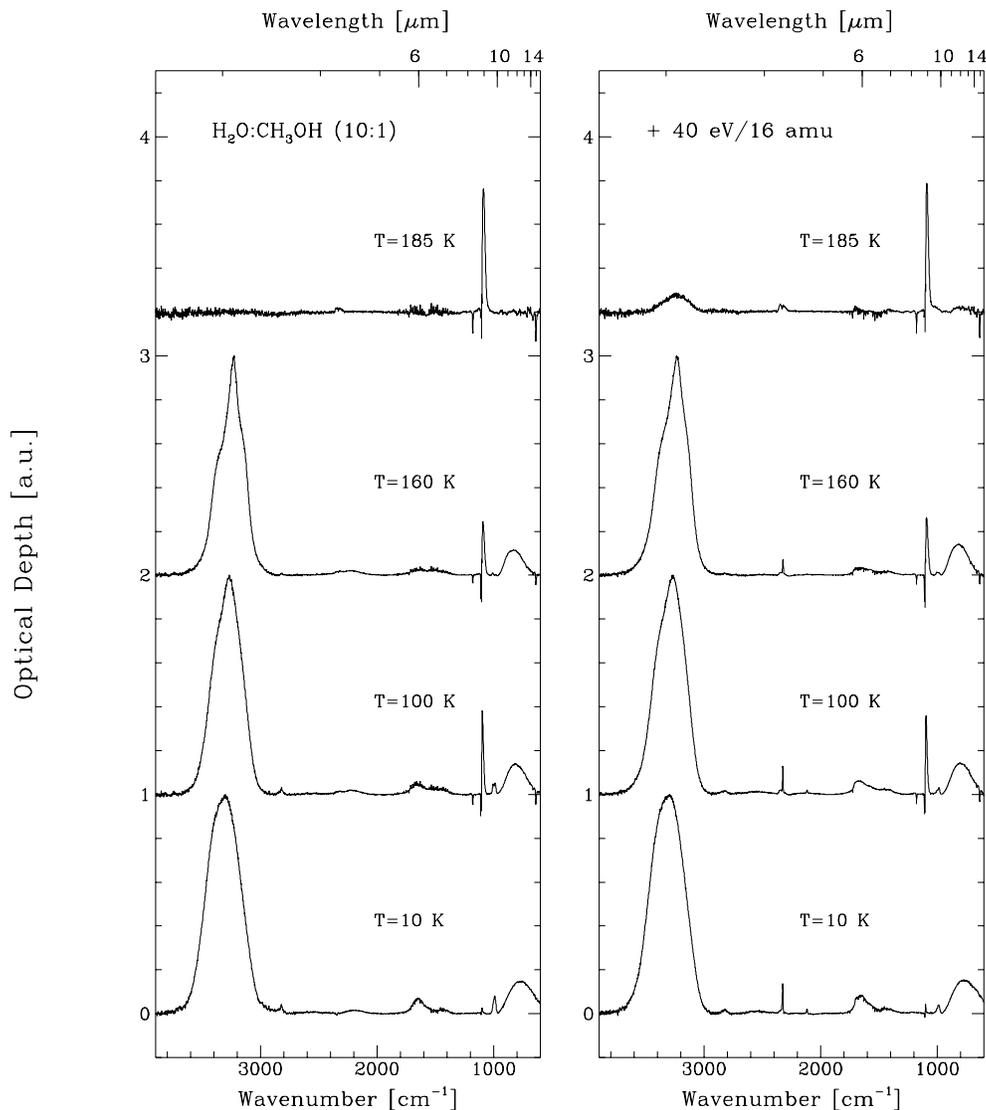
Fig. 10. IR spectra of an unirradiated H_2O:CH_3OH (10:1) mixture are compared, at different temperatures (T = 10–180 K), with those of the irradiated mixture (40 eV/16amu). Spectra are normalized to the 3260 cm^{-1} band

ice with 30–40 eV/16amu, estimation of the CH_3OH/H_2O ratio from the 1460 and 2830 cm^{-1} bands would differ of a factor 3–4.

When abundances of solid species are estimated from astronomical spectra, the main hypothesis made is that the physical and chemical properties of the ice on interstellar grains are the same as that of a laboratory sample then it is possible to use the integrated absorbances as measured in laboratory. However it is not well known how icy grain mantles form and then which is the structure of interstellar ices.

Laboratory experiments here presented have shown that ion irradiation causes a modification of both the physical and chemical properties of an icy sample and that the integrated absorbances measured for unprocessed ices are no longer appropriate. In this view the different estimation of methanol abundance depending on which band is used to compute it could not be a problem any more.

However these hypotheses have to be confirmed by further experiments and by a detailed and simultaneous comparison of laboratory data of irradiated samples with astronomical spectra of all the methanol bands detected along the same line of sight. This will be possible when ISO data are available to the scientific community.

References

Allamandola L.J., Sandford S.A., Valero G.J., 1988, Icarus 76, 225

Allamandola L.J., Sandford S.A., Tielens A.G.G.M., Herbst T.M., 1992, ApJ 399, 134

Baratta G.A., Palumbo M.E., 1998, J. Opt. Soc. Am. A 15, 3076

Baratta G.A., Leto G., Spinella F., Strazzulla G., Foti G., 1991, A&A 252, 421

Baratta G.A., Castorina A.C., Leto G., et al., 1994, Planet. Space Sci. 42, 759

Chiar J.E., Adamson A.J., Whittet D.C.B., 1996, ApJ 472, 665

Gerakines P.A., Schutte W.A., Ehrenfreund P., 1996, A&A 312, 289

Greenberg J.M., 1982, What are comets made of? A model based on interstellar dust. In: Wilkening L.L. (ed.) Comets. The Univ. of Arizona Press, Tucson

Grim R.J.A., Greenberg J.M., Schutte W., Schmitt B., 1989, ApJ 341, L87

Grim R.J.A., Baas F., Geballe T.R., Greenberg J.M., Schutte W., 1991, A&A 243, 473

Hudgins D.M., Sandford S.A., Allamandola L.J., Tielens A.G.G.M., 1993, ApJ Suppl. Ser. 86, 713

Hudson R.L., Moore M.H., 1995, Radiat. Phys. Chem. 45, No. 5, 779

Jenniskens P., Baratta G.A., Kouchi G.A., et al., 1993, A&A 273, 583

Moore M.H., Ferrante R.F., Nuth J.A., 1996, PlSpSci 44, 927

Mulas G., Baratta G.A., Palumbo M.E., Strazzulla G., 1998, A&A 333, 1025

Palumbo M.E., 1997, Adv. Space Res. 20, 8, 1637

Palumbo M.E., Strazzulla G., 1993, A&A 269, 568

Palumbo M.E., Tielens A.G.G.M., Tokunaga A.T., 1995, ApJ 449, 674

Palumbo M.E., Geballe T.R., Tielens A.G.G.M., 1997, ApJ 479, 839

Palumbo M.E., Baratta G.A., Brucato J.R., et al. 1998, A&A 334, 247

Pendleton Y. J., Tielens A.G.G.M., Werner M.W., 1990, ApJ 349, 107

Sandford S.A., Allamandola L.J., 1993, ApJ 417, 815

Schutte W.A., Tielens A.G.G.M., Sandford S.A., 1991, ApJ 382, 523

Schutte W.A., Gerakines P.A., Geballe T.R., van Dishoeck E.F., Greenberg J.M., 1996a, A&A 309, 633

Schutte W.A., Tielens A.G.G.M., Whittet D.C.B., et al. 1996b, A&A 315, L333

Skinner C.J., Tielens A.G.G.M., Barlow M.J., Justtanont K., 1992, ApJ 399, L79

Spinella F., Strazzulla G., Baratta G.A., 1991, Rev. Sci. Instrum. 62, 1743

Strazzulla G., Baratta G.A., 1991, A&A 241, 310

Strazzulla G., Johnson R.E., 1991, Irradiation effects on comets and cometary debris. In: Newburg R. Jr., Neugebaur M., Rahe J. (eds.), Comets in the Post-Halley Era. Kluwer Dordrecht, p. 243

Strazzulla G., Castorina A.C., Palumbo M.E., 1995, Planet. Space Sci. 43, 1247

Teixeira T.C., Emerson J.P., Palumbo M.E., 1998, A&A 330, 711

Tielens A.G.G.M., 1989, Dust in Dense Clouds. In: Tielens A.G.G.M., Allamandola L.J. (eds.), Interstellar Dust. IAU, p.239

Tielens A.G.G.M., Allamandola L.J., 1987, Evolution of Interstellar Dust. In: Morfill G.E., Scholer M. (eds.), Physical Process in Interstellar Clouds. Reidel Dordrecht, p. 333

Tielens A.G.G.M., Allamandola L.J., Bregman J., et al., 1984, ApJ 287, 697

Tielens A.G.G.M., Tokunaga A.T., Geballe T.R., Baas F., 1991, ApJ 381, 181