Class II maser candidates in substituted methanol: CH$_3$OD, $^{13}$CH$_3$OH, CH$_3^{18}$OH and CH$_3$SH

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ABSTRACT
We investigate the possibility of interstellar masers in transitions of the methanol isotopomers CH$_3$OD, $^{13}$CH$_3$OH and CH$_3^{18}$OH, and of CH$_3$SH. The model used, in which masers are pumped through the first and second torsionally excited states by IR radiation, has accounted successfully for the Class II masers in main species methanol, $^{12}$CH$_3^{16}$OH. Several potential maser candidates are identified for CH$_3$OD, their detectability depending on the enrichment of this species in star-forming regions. In $^{13}$CH$_3$OH and CH$_3^{18}$OH the best maser candidates are direct counterparts of the well-known 6.7- and 12.2-GHz methanol masers, but the lower interstellar abundance of these substituted species means that the expected brightness is greatly reduced. The maser candidates in CH$_3$SH are also weak. By comparing these species we find that the large b-component of the dipole moment in methanol plays a significant role in its propensity to form masers, as does the strong torsion–rotation interaction due to the light hydroxyl frame. Thus the exceptional brightness of interstellar methanol masers is due to a favourable combination of molecular properties as well as high interstellar abundance.

Key words: masers – stars: formation – ISM: abundances – ISM: molecules – radio lines: ISM.

1 INTRODUCTION

Strong interstellar masers have become a useful probe of star-forming regions, because of their brightness, and because of their special excitation requirements, which can be found in the neighbourhoods of newly formed massive stars. Maser lines of OH, H$_2$O and CH$_3$OH are the most widespread tracers of such regions (reviewed by Elitzur 1992). NH$_3$ and H$_2$CO masers occur in a small number of sources (Madden et al. 1986; Mehringer, Goss & Palmer 1995). In each of these molecules the maser lines can be seen as a consequence of special features of the energy-level structure and selection rules, which allow population inversions to develop in a small minority of the vast number of interstellar lines. Masing molecular species are also all of relatively high interstellar abundance in such regions, providing sufficient column density along the maser-amplifying path to generate exceptionally bright lines (e.g. brightness temperatures > 10$^{10}$ K).

The molecule with the greatest number of different maser transitions is methanol, CH$_3$OH. Strong methanol masers have been divided by observers into two classes, Class I and Class II (Menten 1991). The Class II methanol masers, of which the 6.7-GHz $^1_1$A$^+$ and 12.2-GHz $^2_2$F$^2_2$ lines are the most notable examples, are generally found in association with ultracompact H II regions and other indicators of massive star formation. A model involving pumping by IR radiation to the first and second torsionally excited states has successfully accounted for the extreme brightness of these lines (Sobolev & Deguchi 1994a; Sobolev, Cragg & Godfrey 1997a, hereafter SCG97a), and also for the occurrence of Class II masers in a further 16 transitions of methanol (Sobolev, Cragg & Godfrey 1997b, hereafter SCG97b). The transitions which form Class II masers are often seen in absorption in Class I sources, and vice versa. This is associated with the presence or absence of a continuum radiation field with temperature higher than the gas kinetic temperature (Cragg et al. 1992).

In this paper we apply the same excitation model to four closely related species: CH$_3$OD, $^{13}$CH$_3$OH, CH$_3^{18}$OH and CH$_3$SH. In the following we refer to the main isotopic species, $^{12}$CH$_3^{16}$OH, as methanol. Each of the substituted species has a hindered rotor spectrum similar to that of methanol, with low-lying torsionally excited states, and the same maser pumping mechanism will therefore be effective. The interstellar abundance of the substituted species is much lower than that of methanol. However, detection of the NH$_3$ maser line (Mauersberger, Wilson & Henkel 1986; Gaume et al. 1991) shows that molecules containing rarer isotopes
can manifest detectable emission with maser characteristics. We aim to identify potential maser candidates in the substituted methanol species, if such exist at plausible values of column density, and so provide further observational constraints for determination of physical parameters by modelling.

The modelling of five structurally related species also provides an opportunity to examine the effects of small differences in molecular properties on the maser calculations, and so to clarify the features of methanol which govern its propensity for maser action.

More than 20 lines of CH$_3$OD have been identified in interstellar molecular clouds (Lovas 1992). In Orion-KL the relative abundance of CH$_3$OD to CH$_3$OH was found to be in the range 1/100–1/17 (Mauersberger et al. 1988), enhanced by a factor of $\sim$1000 over the interstellar D/H ratio. The presence of CH$_3$OD in enriched abundance in star-forming regions is taken as strong evidence for the production of gas-phase methanol by the evaporation of grain mantles formed at low temperatures (Jacq et al. 1993), in which the deuterium enrichment is a legacy of low-temperature ion–molecule reactions.

Approximately 50 lines of $^{13}$CH$_3$OH have been seen in SgrB2 and OriMC-1 (Lovas 1992). The abundance ratio to the main species was found to be 1/32 in SgrB2 (Turner 1991) and 1/17 in OMC-1 (Sutton & Herbst 1988). The 14.8-GHz $2_0 \rightarrow 3_1 E$ transition of $^{13}$CH$_3$OH was seen in absorption in SgrB2 (Kuiper et al. 1989), in accord with the strong absorption seen in the 12.2-GHz $2_0 \rightarrow 3_1 E$ methanol transition (Whiteoak et al. 1988) in this Class I source. The relative abundance of $^{13}$CH$_3$OH to $^{12}$CH$_3^{16}$OH was estimated at 1/40 in this case. Absorption in this transition signals similar excitation to that of the main species, so that maser emission might be expected in Class II sources. However, Menten & Batrla (1989) were unable to detect $^{13}$CH$_3$OH $2_0 \rightarrow 3_1 E$ emission in NGC 6334 at a level of 1/2000 of the intensity of the methanol maser.

The 11.6-GHz $2_0 \rightarrow 3_1 E$ transition of CH$_3^{18}$OH was also seen in absorption in SgrB2 (Gardner et al. 1989), with abundance relative to the main species estimated as 1/210. Again this is indicative of similar excitation to methanol. We are not aware of any other interstellar detections of this species. Abundance ratios of $^{16}$O/$^{18}$O $\approx$ 1/250 are typical of the Galactic Centre region, but elsewhere the ratio is more likely to be $\sim$1/500 (e.g. Wilson & Matteucci 1992).

Some 20 lines of CH$_3$SH have been observed in interstellar molecular clouds, again in the sources SgrB2 and OriMC-1 (Lovas 1992). The abundance of this species in SgrB2 is estimated to be approximately 1/31 of that of methanol (Turner 1991).

2 ENERGY LEVELS AND TRANSITIONS

The rotational spectrum of methanol is characterized as that of a slightly asymmetric prolate rotor with hindered internal rotation of the methyl group. The first excited state of the torsional vibration is only 200 cm$^{-1}$ above the ground state, low enough to be populated at interstellar temperatures (e.g. Menten et al. 1986). The degree of torsion–rotation interaction is considerable, leading to a complex spectrum which is best fitted by the Internal Axis Method (IAM) Hamiltonian (Herbst et al. 1984). Energy levels are labelled by the torsional angular momentum quantum number $v_t$, the rotational angular momentum quantum number $J$, its projection on the molecule fixed axis $k$, and a symmetry label $A^+$ or $A^-$ (Lees & Baker 1968).

Fig. 1 displays the methanol energy levels for $v_t = 0$–2, $J = 0$–12, $E$ species, as used in the Class II maser excitation calculations. Energies are calculated from the IAM Hamiltonian of De Lucia et al. (1989). There are no radiative or significant collisional transitions connecting the $E$ and $A$ symmetry species, which are therefore modelled separately. The selection rules for radiative transitions permit $\Delta J = -1, 0, +1$ (known as P-, Q- and R-branch respectively) and $\Delta k = 0, \pm 1$ (known as $a$- and $b$-type respectively after the associated dipole moment component) transitions. The selection rules are further discussed in Cragg et al. (1993). The observed Class II methanol masers are all $b$-type transitions in the torsional ground state.

Similar IAM treatments have been applied to the spectra of CH$_3$OD (Anderson et al. 1988), $^{13}$CH$_3$OH (Anderson, Herbst & De Lucia 1987), CH$_3^{18}$OH (Hoshino et al. 1996) and CH$_3$SH (Sastry et al. 1986). The calculated energy levels for CH$_3$OD and CH$_3$SH are also displayed in Fig. 1. On this scale the energy-level diagrams for $^{13}$CH$_3$OH and CH$_3^{18}$OH are indistinguishable from that of CH$_3$OH. However, it is apparent that the S and D substitutions produce considerable differences in the pattern of energy levels and the spectra. As Fig. 1 illustrates, both CH$_3$OD and CH$_3$SH have more regularly spaced $k$-ladders than $^{12}$CH$_3^{16}$OH in the torsionally

Figure 1. IAM energy levels for the ground, first and second torsionally excited states of $E$-species CH$_3$OH, CH$_3$OD and CH$_3$SH.
excited states. This is also true of the ground state, with the result that the P-branch $2_{\jmath} - 3_{\jmath-1}E$ and $5_{1} - 6\Delta A^+$ transitions are reversed to the R-branch transitions $3_{\jmath-1} - 2_{\jmath}E$ and $6_{1} - 5\Delta A^+$. The frequencies of these transitions for the five species are given in Table 1.

The reason for such dramatic shifts in the position of the energy levels can be traced back to the amplitude of variation of the torsional eigenvalues with $k$ quantum number, as illustrated in Fig. 2. Because of strong torsion–rotation interaction, the torsional eigenvalues influence the position of the $J = 0$ origin of each $k$-ladder, which is perturbed from the asymmetric rotor distribution in all these species, but most noticeably so in methanol. These torsional eigenvalues are determined by the IAM parameters $F$ and $\rho$ (Table 2), which in turn are a function of the relative moments of inertia of the top and frame components of the molecule.

Using the fitted IAM parameters of the authors referred to above, we have calculated the Einstein $A$ coefficients for all transitions $J = 0–12$, $v_1 = 0–2$ for the species CH$_3$OD, $^{13}$CH$_3$OH, CH$_3^{18}$OH and CH$_3$SH, in the same way as was done for methanol by Cragg et al. (1993). The dipole moment components used in these calculations are given in Table 2. We also calculated Einstein coefficients for a hypothetical hybrid molecule with the energies and line strengths of CH$_3$SH but the dipole moment components of methanol, to investigate the relative importance of these factors.

### Table 1. Calculated IAM frequencies (MHz) for methanol maser counterpart transitions in methanol isotopomers and CH$_3$SH. A negative frequency indicates that the transition is reversed from P- to R-branch.

<table>
<thead>
<tr>
<th>species</th>
<th>$2_{\jmath} - 3_{\jmath-1}E$</th>
<th>$5_{1} - 6\Delta A^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$CH$_3^{16}$OH</td>
<td>12179</td>
<td>6668</td>
</tr>
<tr>
<td>CH$_3$OD</td>
<td>-154964</td>
<td>-148360</td>
</tr>
<tr>
<td>$^{13}$CH$_3$OH</td>
<td>14783</td>
<td>14300</td>
</tr>
<tr>
<td>CH$_3^{18}$OH</td>
<td>11630</td>
<td>15134</td>
</tr>
<tr>
<td>CH$_3$SH</td>
<td>-141150</td>
<td>-49785</td>
</tr>
</tbody>
</table>

Figure 2. Torsional eigenvalues for the ground torsional state of $E$-species CH$_3$OH, CH$_3$OD and CH$_3$SH.

### Table 2. Dipole moment components ($\mu$) and IAM torsional parameters ($F$ and $\rho$) for methanol isotopomers and CH$_3$SH. A species parameters are tabulated in cases where the symmetry species were fitted separately.

<table>
<thead>
<tr>
<th>species</th>
<th>$\mu_\alpha$</th>
<th>$\mu_\beta$</th>
<th>$\mu$ reference</th>
<th>$F$ cm$^{-1}$</th>
<th>$\rho$</th>
<th>IAM reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$CH$_3^{18}$OH</td>
<td>0.896</td>
<td>1.412</td>
<td>Sastry et al. (1981)</td>
<td>27.6337</td>
<td>0.8097</td>
<td>De Lucia et al. (1989)</td>
</tr>
<tr>
<td>CH$_3$OD</td>
<td>0.833</td>
<td>1.488</td>
<td>Kaushick et al. (1980)</td>
<td>17.4509</td>
<td>0.6997</td>
<td>Anderson et al. (1988)</td>
</tr>
<tr>
<td>$^{13}$CH$_3$OH</td>
<td>0.89</td>
<td>1.44</td>
<td>Ivash (1952)</td>
<td>27.6273</td>
<td>0.8097</td>
<td>Anderson et al. (1987)</td>
</tr>
<tr>
<td>CH$_3^{18}$OH</td>
<td>0.896</td>
<td>1.412</td>
<td>assumed</td>
<td>27.4209</td>
<td>0.8082</td>
<td>Hoshino et al. (1996)</td>
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<tr>
<td>CH$_3$SH</td>
<td>1.312</td>
<td>0.758</td>
<td>Nakagawa &amp; Johns (1989)</td>
<td>15.0696</td>
<td>0.6523</td>
<td>Sastry et al. (1986)</td>
</tr>
</tbody>
</table>

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abundance. We can thus identify the most promising candidates, and then ask whether they are likely to be observable at more plausible abundance levels. The calculations were therefore performed for both $A$ and $E$ species for a range of specific column densities $N_M/\Delta V = 10^9$ to $10^{13}$ cm$^{-3}$ s.

From the thousands of transitions in each species, we have extracted those which attain predicted brightness temperature $> 10^4$ K over the range of column densities considered. All of these transitions have negative optical depth due to population inversion, and are therefore categorized as masers. Promising maser candidates for observation should become bright over a wide range of model parameters. The tiny spot sizes observed for methanol masers (Menten et al. 1988a,b, 1992) mean that brightness temperatures $< 10^5$ K are likely to be difficult to detect in low-resolution observations due to very small filling factors. In particular, it may be difficult to distinguish such maser signals from broadly distributed weak thermal emission.

![Figure 3. CH$_3$OD model spectra at specific column density $N_M/\Delta V = 10^{11}$ cm$^{-3}$ s, in the low ($n_H = 10^5$ cm$^{-3}$) and high ($n_H = 10^7$ cm$^{-3}$) density regimes. See text for values of other model parameters.](image-url)

### Table 3. Model brightness temperatures for CH$_3$OD as displayed in Fig. 3. All transitions with brightness temperatures $> 10^4$ K are shown bold for emphasis. Frequencies quoted to 10 kHz are laboratory frequencies (Anderson, Herbst & De Lucia 1993) accurate to 50–100 kHz, while frequencies quoted to 1 MHz are calculated according to Anderson et al. (1988).

<table>
<thead>
<tr>
<th>$v_1$</th>
<th>Transition</th>
<th>Freq MHz</th>
<th>log($T_B$/K)</th>
<th>$v_1$</th>
<th>Transition</th>
<th>Freq MHz</th>
<th>log($T_B$/K)</th>
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<td>3(2)A$^-$</td>
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<tr>
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<td>11(−2)E</td>
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<td>4.5</td>
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</table>

### Figure 4. Model brightness temperatures for selected Class II maser candidates in CH$_3$OD as a function of specific column density. The selected transitions illustrate both masers which become extremely bright at very high CH$_3$OD column densities, and also more moderate $J_{A^−}$ $J_{A^+}$ masers which remain significant at lower column densities. Calculations are performed at high ($n_H = 10^5$ cm$^{-3}$) and low ($n_H = 10^3$ cm$^{-3}$) densities of hydrogen. Transition frequencies are given in Table 3.

4 RESULTS
In CH$_3$OD the set of transitions which become Class II masers in the model differs substantially from that of CH$_3$OH. In Fig. 3 we display model spectra for CH$_3$OD in the high- and low-density regimes for specific column density $10^{11}$ cm$^{-3}$ s. With the deuterium enrichment seen in Orion-KL, this would correspond to very large specific column density of CH$_3$OH in the range $10^{12.2}$ to $10^{13}$ cm$^{-3}$ s. The transitions which feature in this spectrum are identified in Table 3. This spectrum is presented to illustrate the production of CH$_3$OD masers at large model values of specific column density.
and over-estimates the brightness temperatures that can be reasonably expected for this species.

The model brightness temperature for several of the lines which feature strongly in the spectrum in Fig. 3 are shown as a function of model specific column density. Calculations are performed at high $(n_H = 10^5 \text{cm}^{-3})$ and low $(n_H = 10^3 \text{cm}^{-3})$ densities of hydrogen. Transitions are labelled by calculated IAM frequencies (MHz).

![Figure 5. Counterparts of the 6.7- and 12.2-GHz methanol masers in $^{13}$CH$_3$OH and CH$_3^{18}$OH, as a function of model specific column density. Calculations are performed at high $(n_H = 10^5 \text{cm}^{-3})$ and low $(n_H = 10^3 \text{cm}^{-3})$ densities of hydrogen. Transitions are labelled by calculated IAM frequencies (MHz).](https://academic.oup.com/mnras/article-abstract/300/4/999/988342)

At a CH$_3$OD specific column density $< 10^{11} \text{ cm}^{-3}$ s the model brightness temperatures fall away very rapidly for most of the maser candidate transitions. An exception to this is the Q-branch series of transitions $J_aA^- - J_bA^+$ around 140 GHz, which do not attain such extreme brightness at very high column density (Fig. 4), but remain significant down to CH$_3$OD column density $10^{10} \text{ cm}^{-3}$ s. This curve is similar in shape to that found in modelling the 157-GHz $J_0 - J_1 E$ Q-branch methanol masers observed by Slysh, Kalenskii & Val’ts (1995), which also differ in their model dependence on specific column density from the more numerous P-branch masers. Since specific column densities as large as $10^{11} \text{ cm}^{-3}$ s for CH$_3$OD are unlikely, the $J_aA^- - J_bA^+$ series of transitions appear to be the best candidates for observation of Class II masers in this species, with model brightness temperatures up to $10^6 \text{ K}$ at CH$_3$OD specific column density $10^{10.3} \text{ cm}^{-3}$ s.

Several members of the $J_aA^- - J_bA^+$ series of transitions in CH$_3$OD were included in the survey of Mauersberger et al. (1988). The detection of maser emission in these lines is complicated by the fact that they are also relatively strong in quasi-thermal sources such as Orion-KL, where the $J = 4, 5, 6, 7$ and 8 members of the series were observed. There is some evidence for anomalous excitation of the $5_1A^- - 5_0A^+$ transition in G 34.3+0.2, while the $2_1 - 2_0E$ and $4_1 - 4_0E$ lines (which are not good maser candidates in our model) were not detected at 0.2 K. The G 34.3+0.2 line was observed towards a position half a beamwidth away from a 6-GHz methanol maser (Caswell et al. 1995), and with $V_{lsr}$ corresponding to that of the methanol maser peak. Although the $4_1A^- - 4_0A^+$ and $5_1A^- - 5_0A^+$ lines were sought by Mauersberger et al. in several other sources, the positions observed were offset sufficiently from methanol maser positions that the evidence for or against masers is inconclusive.

As expected from the earlier discussion of energy-level diagrams, only $^{13}$CH$_3$OH and CH$_3^{18}$OH display counterparts of the 12.2-GHz $2_0 - 3_1E$ and 6.7-GHz $5_1 - 6_0A^+$ methanol masers. Model brightness temperatures over a range of specific column densities for these transitions are displayed in Fig. 5, with the model results for methanol for comparison. It can be seen that the maser excitation in each case is very similar. The 6.7-GHz methanol transition has an advantage in the saturated limit due to its lower frequency, since saturation comes into effect at higher values of brightness temperature (proportional to $\nu^{-2}$) when other factors are equal. Thus, if $^{13}$CH$_3$OH existed in the same interstellar abundance as $^{12}$CH$_3^{16}$OH, we would expect to see $2_0 - 3_1E$ masers at 14.8 GHz of comparable brightness to the methanol 12.2-GHz masers, and $5_1 - 6_0A^+$ transitions at 14.3 GHz somewhat weaker than the 6.7-GHz methanol masers. Likewise, if CH$_3^{18}$OH existed in comparable abundance to $^{12}$CH$_3^{16}$OH, we would expect to see equivalent 11.6-GHz $2_0 - 3_1E$ and 15.1-GHz $5_1 - 6_0A^+$ masers. There are, however, no corresponding maser candidates in CH$_3$OD or CH$_3$SH.

More realistically, if the interstellar abundance of $^{13}$CH$_3$OH is 1/30 that of $^{12}$CH$_3^{16}$OH, we can expect the maser brightness of the 14.3-GHz $5_1 - 6_0A^+$ and 14.8-GHz $2_0 - 3_1E$ lines to be reduced by a large factor over their 6.7- and 12.2-GHz methanol counterparts. The magnitude of this factor will depend on how far into the saturated regime the methanol masers lie. For example, in the high-density calculations illustrated in Fig. 5 with methanol specific column density $10^{11.5} \text{ cm}^{-3}$ s, the model brightness temperatures are $10^{12.1} \text{ K}$ for the 6.7-GHz $5_1 - 6_0A^+$ transition and $10^{12.9} \text{ K}$ for the 12.2-GHz $2_0 - 3_1E$ transition, and both lie near the start of the saturated regime. However, at specific column density $10^{10} \text{ cm}^{-3}$ s the equivalent 14.3- and 14.8-GHz $^{13}$CH$_3$OH counterparts lie in the unsaturated maser regime, with model brightness temperatures $10^{4.5}$ and $10^{4.2} \text{ K}$ respectively, a reduction of some 8 orders of magnitude! This can be considered a worst case estimate, since the difference in abundance of the two species spans the exponential growth region of the maser curve (Fig. 5). Sources in which the methanol masers are thought to be heavily saturated offer better prospects for detection of corresponding masers in the substituted species. Although methanol masers have been observed with flux density as great as 3000 Jy (Norris et al. 1993), detection of corresponding transitions of $^{13}$CH$_3$OH presents a challenge. It is not surprising that Menten & Batrla (1989) found no 14.8-GHz maser in NGC 6334 at 1/2000 the intensity of the methanol maser.

Similarly, if the interstellar abundance of CH$_3^{18}$OH is a factor of 210 lower than that of $^{12}$CH$_3^{16}$OH, we can expect the brightness of the 11.6-GHz $2_0 - 3_1E$ and 15.1-GHz $5_1 - 6_0A^+$ lines to be reduced by an even larger factor over their 6.7- and 12.2-GHz methanol counterparts. For example, at a specific column density of...
CH$_3^{18}$OH 10$^{9.2}$ cm$^{-3}$ s the model brightness temperature of these masers is $\approx$10$^{3.5}$ K. Beam dilution will make such lines extremely difficult to detect, even in bright Class II sources.

For both $^{13}$CH$_3$OH and CH$_3^{18}$OH the $2_0 - 3_1 A^\pm E$ and $5_1 - 6_0 A^\pm$ transitions are by far the best maser candidates, since they attain the highest model brightness over the widest range of parameters, as they do in methanol. Other potential maser transitions are again counterparts of those in the main species. Although it is the $2_0 - 3_1 A^\pm E$ transitions of both species which have been detected in absorption in the Class I source SgrB2, the $5_1 - 6_0 A^\pm$ transitions offer the best prospect for detection as Class II masers.

The CH$_3$SH model spectrum is interesting for the absence of very bright masers, even at equivalent abundance to methanol. This is initially surprising, given the structural similarities of the two species, and the reasons are explored below. Fig. 6 shows the best CH$_3$SH maser candidates, as a function of specific column density. These include the 3.0-GHz $3_1 - 4_0 A^\pm$ counterpart of the 107.0-GHz methanol maser (Val’itsu et al. 1995), and the $J_1 A^\pm - J_0 A_+$ series around 110 GHz which also featured in the predicted spectrum of CH$_3$OD (Fig. 3). At 1/30 methanol abundance the 3.0-GHz line in low-density sources, with model brightness temperature 10$^6$ K at CH$_3$SH specific column density 10$^{10}$ cm$^{-3}$ s, offers the best prospect of detection.

5 DISCUSSION

The results presented demonstrate that the lower relative abundance of the methanol analogues is likely to severely limit maser amplification in these species. Nevertheless, it is interesting to ask how they would behave if they were equally abundant to methanol, in order to reveal the molecular properties which underlie the production of Class II masers. For example, a comparison of the model results for CH$_3$OH and CH$_3$SH illustrates the sensitivity of the maser process to the value of the dipole moment.

The CH$_3$SH maser candidates do not display such dramatic exponential growth to extreme brightness temperatures as seen for the other species over the same range of column densities. Such behaviour does, however, appear when the range of model column densities is extended beyond 10$^{12}$ cm$^{-3}$ s (Fig. 7). This indicates that the spectrum of CH$_3$SH is not fundamentally different from that of CH$_3$OH, and both are capable of producing very bright Class II masers under the right conditions, although such conditions occur in the interstellar medium for methanol only.

Apart from being present in larger interstellar abundance than CH$_3$SH, CH$_3$OH also has the advantage of a larger $\mu_b$ dipole moment component and stronger torsion–rotation interaction (Table 2). These factors both affect the radiative pumping rates, via the $\mu_b^2$ and $\nu^3$ factors respectively in the Einstein $A$ coefficients. The relative importance of these factors in the generation of the masers can be gauged from model calculations for a hypothetical hybrid molecule with the CH$_3$SH energy-level structure and line strengths, but CH$_3$OH dipole moment components. Such calculations do indeed produce bright masers comparable to many of those seen in methanol, and over the same range of specific column densities. An example is shown in Fig. 7. However, the best maser in the hybrid molecule still fails to match the 6.7-GHz methanol maser.

The dipole moment components influence the development of masers in the model in three ways. First, the brightness of the $b$-type maser lines is proportional to $\mu_b^2$ via the Einstein $A$ coefficient in the unsaturated maser regime. This is the dominant effect, as illustrated in Fig. 7 where substituting the methanol dipole moment components has a comparable effect to increasing the specific column density by a factor $\sim$3 in low-density calculations. Secondly, the dipole moment influences the overall balance between radiative and collisional processes, so that the CH$_3$SH masers are quenched at a lower hydrogen density. Thirdly, the change in relative transition strengths influences the pumping of individual lines, and this is most noticeable in the Q-branch transitions.

No masers in the hybrid molecule are as bright over a wide range of model conditions as the 6.7-GHz methanol maser. This is also true of CH$_3$OD, despite it having a larger $\mu_b$ than methanol. We conclude that while the dipole moment of methanol plays a strong role in the generation of the interstellar Class II masers, other features of the pumping scheme govern the production of the brightest masers.

Studies of the radiative pumping mechanism in this model (Sobolev & Deguchi 1994b) have demonstrated the importance of...
the $\nu_1 = 0 \rightarrow 2$ transitions in the generation of population inversions within the ground state. Since these transitions have the selection rule $\Delta k = \pm 1$, irregularities in the distribution of the $k$-ladders in the torsionally excited states lead to substantial differences in the frequencies of pumping transitions for nearby energy levels in the ground state. Favourable combinations can lead to the development of population inversions. In CH$_3$OD and CH$_3$SH the $k$-ladders in the torsionally excited states are more regularly distributed than in methanol (Fig. 1), because of differences in the relative moments of inertia of the two ends of the molecule. This is ultimately responsible for the absence in these species of the same bright and widespread nature as the 6.7-GHz methanol maser, even after the differences in abundance and dipole moment are artificially taken into account.

Thus CH$_3$SH is a poor Class II maser molecule, not only because of its lower interstellar abundance in comparison with methanol, but also because the substitution of O by S leads to a subtle differences in the spectrum and transition rates. Due to the exponential nature of maser amplification, these translate into many orders of magnitude difference in the propensity to form strong masers.

6 CONCLUSIONS

The best maser candidates for observation in Class II methanol maser sources have been identified for several related species. These are the $J_{A^+} - J_{0^+}$ series in the range 130–160 GHz for CH$_3$OD, the $S_1 - 6_0A^+$ counterpart of the 6.7-GHz methanol maser for $^{13}$CH$_3$OH at 14.3 GHz and CH$_3^{18}$OH at 15.1 GHz, and the 3.0 GHz $S_1 - 4_0A^+$ line for CH$_3$SH. The detectability of such masers depends greatly on the abundance of these species in star-forming regions, and on the degree of beam dilution in the observation. It is expected that CH$_3$OD offers the best prospect of observing a Class II maser in a species other than $^{13}$CH$_3^{16}$OH, if its relative abundance is indeed enhanced by the evaporation of grain mantles formed from low-temperature deuterium-enriched gas. Masers of $^{13}$CH$_3$OH are likely to be more readily detected than masers of CH$_3$SH, while CH$_3^{18}$OH masers offer the least prospect of detection due to the low relative abundance of this species.

The origin of the methanol maser phenomenon is further clarified by a comparison of the masers generated in model calculations for these structurally related species. While it is likely that only methanol is found with sufficient column density to permit extensive maser amplification, the particular effectiveness of IR radiative pumping in generating population inversions in methanol is also a result of its fundamental molecular properties. Thus the widespread existence of the very bright 6.7-GHz methanol maser in star-forming regions stems not only from enriched methanol abundance, but also from fundamental features of the structure of this molecule, concerned with its polarity and internal rotation.

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