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Detection of doubly-deuterated methanol in the solar-type protostar IRAS 16293−2422

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Abstract. We report the first detection of doubly-deuterated methanol (CHD_2OH), as well as firm detections of the two singly-deuterated isotopomers of methanol (CH_2DOH and CH_3OD), towards the solar-type protostar IRAS 16293−2422. From the present multifrequency observations, we derive the following abundance ratios: $[CHD_2OH]/[CH_3OH] = 0.2 \pm 0.1$, $[CH_2DOH]/[CH_3OH] = 0.9 \pm 0.3$, $[CH_3OD]/[CH_3OH] = 0.04 \pm 0.02$. The total abundance of the deuterated forms of methanol is greater than that of its normal hydrogenated counterpart in the circumstellar material of IRAS 16293−2422, a circumstance not previously encountered. Formaldehyde, which is thought to be the chemical precursor of methanol, possesses a much lower fraction of deuterated isotopomers (∼20%) with respect to the main isotopic form in IRAS 16293−2422. The observed fractionation of methanol and formaldehyde provides a severe challenge to both gas-phase and grain-surface models of deuteration. Two examples of the latter model are roughly in agreement with our observations of CHD_2OH and CH_2DOH if the accreting gas has a large (0.2–0.3) atomic D/H ratio. However, no gas-phase model predicts such a high atomic D/H ratio, and hence some key ingredient seems to be missing.

Key words. ISM: abundances – ISM: molecules – stars: formation – ISM: individual: IRAS 16293−2422

1. Introduction

In the last few years, the study of doubly-deuterated molecules in the interstellar medium has gained considerable attention. This field was boosted by the discovery of an extremely large amount ($D_2CO/H_2CO \sim 10\%$) of doubly-deuterated formaldehyde in the low mass protostar IRAS 16293−2422 (hereafter IRAS 16293; Ceccarelli et al. 1998), a fractionation about 25 times larger than in Orion (Turner 1990). Follow-up observational studies of this first discovery confirmed this very large degree of deuteration in IRAS 16293 (Loinard et al. 2000), and allowed a study of its spatial distribution (Ceccarelli et al. 2002). Subsequently, similarly large amounts of doubly-deuterated formaldehyde and ammonia have been observed towards another very young protostellar core, 16293E, which lies in the same molecular cloud (L1689N) as IRAS 16293 (Loinard et al. 2001) and in the molecular cloud L1689N itself (Ceccarelli et al. 2002). Finally, preliminary results of an ongoing project show that it is likely that *all* low-mass protostars present similarly large abundance ratios of doubly deuterated formaldehyde with respect to H_2CO, whereas high-mass protostars do not (Loinard et al. 2002; Ceccarelli et al. 2002).

All these observations suggest that such a large deuteration of formaldehyde is produced during the cold and dense pre-collapse phase of low-mass protostars. Highly deuterated ices are very likely formed via active grain chemistry (Tielens 1983), stored on the grain mantles, and eventually released into the gas during the collapse phase, when the heating of newly-formed protostars evaporates the CO-rich ices (Ceccarelli et al. 2001a). Methanol is also commonly believed to be formed on grain surfaces, because gas-phase models cannot account for the large detected abundances of methanol in hot cores (Menten et al. 1988). If formaldehyde and methanol are produced on grain surfaces by simple successive hydrogenations of CO, then the reproduction of the abundance ratios between deuterated isotopomers and their normal counterparts is a crucial test for the grain-surface theory of deuteration (e.g. Charnley et al. 1997).

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Although the grain picture seems qualitatively consistent with all the observations so far available towards protostars, the nature of the production of deuterated molecular species, whether it occurs completely via active grain chemistry (starting from a high D/H atomic ratio derived from gas-phase chemistry) or at least partially via gas-phase formation, is still largely debated (see for example Roberts & Millar 2000b). The debate has not been settled conclusively because of the relatively small body of available observations and the discovery of relatively large abundances of doubly-deuterated ammonia ($NHD_2/NH_3 \sim 0.001$; Roueff et al. 2000) in the molecular cloud L134N and triply-deuterated ammonia in the low-mass protostar NGC 1333–IRAS 4 (van der Tak et al. 2002) and in the dark cloud B1 (Lis et al. 2002). The observed fractionation of ammonia in L134N can be accounted for by gas-phase models if a high degree of depletion of heavy materials onto the grain mantles is assumed (Roberts & Millar 2000b; Rodgers & Charnley 2001). The ND_3 observations from Lis et al. (2002) can also be explained in the framework of gas-phase chemical models if the dissociative recombination of partially deuterated ions results in a somewhat higher probability for the ejection of hydrogen atoms than for deuterium atoms. We wish to emphasize that this debate is not merely academic, as it involves our understanding of the chemistry of the interstellar medium and of ice formation in general and deuteration processes in particular. Many observational studies use deuteration processes, which are supposedly well-understood, to derive key quantities such as the deuterium abundance (e.g. in the Galactic Center; Lubowich et al. 2000) or the degree of ionization (e.g. in protostars; Williams et al. 1998). The actual state of our comprehension of those processes has therefore a large impact.

In this Letter, we report the very first detection of a doubly-deuterated isotopomer of methanol (CHD_2OH), with 15 detected lines, towards the low-mass protostar IRAS 16293−2422. We also report the detection of the two singly-deuterated forms (CH_2DOH and CH_3OD) of methanol towards the same object. We compare the derived fractionation ratios as well as the formaldehyde fractionation (Loinard et al. 2000) with predictions based on active grain chemistry.

2. Observations and results

Using the IRAM 30-meter telescope (Pico Veleta, Spain), we detected the 23 CH_2DOH lines, 6 CH_3OD lines, and 15 CHD_2OH lines reported in Table 1. The telescope was pointed at the coordinates $\alpha(2000) = 16^h32^m22.6^s$ and $\delta(2000) = -24°28'33.0''$. The observations were performed in November 2001 and May 2002. Four receivers were used simultaneously at 3, 2, 1.3 and 1.1 mm with typical system temperatures of about 100, 200, 400 and 800 K respectively. These receivers were connected to an autocorrelator divided in up to eight units depending on the setting. The telescope beam width varies between 30″ at 83 GHz and 11″ at 226 GHz. All observations were performed using the wobbler switching mode with an OFF position 4′ from the center. The pointing accuracy was monitored regularly on strong extragalactic continuum sources and found to be better than 3″. Our spectra were obtained with integration times ranging from 70 to 400 min for some CHD_2OH lines.

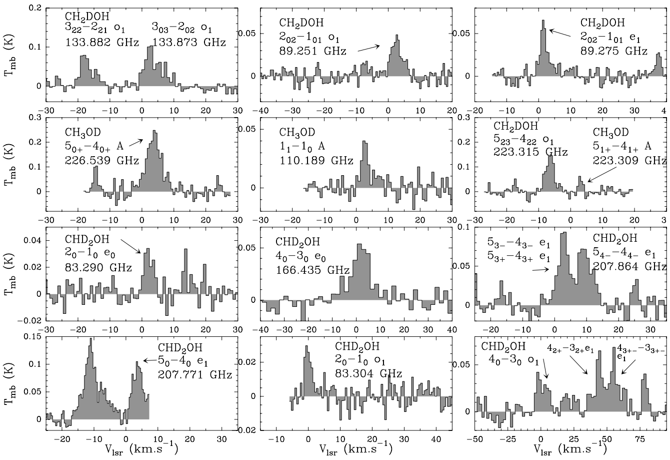

Fig. 1. Examples of CH_2DOH, CH_3OD and CHD_2OH lines. The intensities are reported in main-beam brightness temperature.

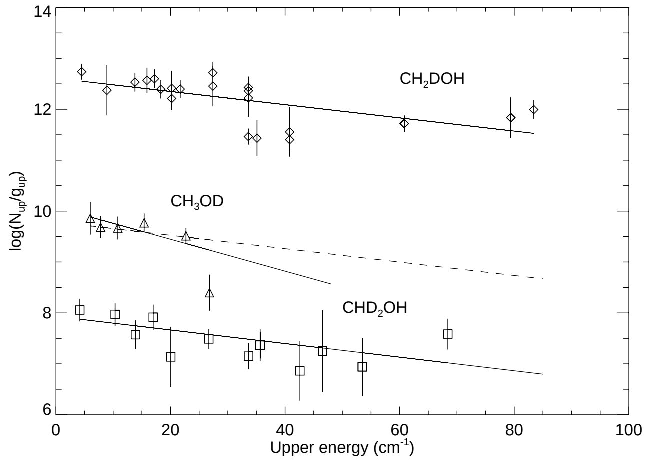

Fig. 2. Rotational diagrams for the observed transitions of CH_2DOH (diamonds), CH_3OD (triangles), and CHD_2OH (squares). For the sake of clarity the CH_3OD and CHD_2OH points have been shifted by −2 and −4, respectively. The dashed line is the result of the fit obtained by fixing the rotational temperature at 47.5 K.

Examples of observed spectra are shown in Fig. 1. The emission was detected at the v_{LSR} of the source, namely 3.9 km s^{-1}. The lines have FWHM of ~5 km s^{-1}, very similar to the linewidths observed for the HDCO and D_2CO lines in IRAS 16293 (Loinard et al. 2000). The measured intensities, linewidths and main-beam temperatures are reported in Table 1.

3. Derivation of the column densities

We derived the total column density of the three species from the rotational diagrams presented in Fig. 2. The observed scattering is likely due to non-LTE and opacity effects. Note that the level column densities are averaged on a 10″ beam, i.e. the smallest beam of our observations, following the suggestion by van Dishoeck et al. (1995) of enhanced methanol emission in the central ≤10″ region of IRAS 16293. The derived rotational temperatures and overall column densities for the

Table 1. Parameters of the observed CH_2DOH, CH_3OD and CHD_2OH transitions. The fluxes were derived using Gaussian fits, and the uncertainty given is $\sqrt{\sigma_{\mathrm{stat}}{}^2 + \sigma_{\mathrm{cal}}{}^2}$ where σ_{stat} is the statistical error and σ_{cal} the calibration uncertainty (15%). The frequencies for CHD_2OH are from Mukhopadhyay (in prep.). The line strengths (given in Deb^2) used to interpret the data are from J. Pearson (private communication) for CH_2DOH, from Anderson et al. (1988) for CH_3OD, and from Mukhopadhyay (1998) for CHD_2OH.

Frequency GHz	Transition	$\mu^2 S$	E_{up} cm^{-1}	$\int T_{\mathrm{mb}}\mathrm{d}v$ K km s^{-1}	T_{mb} K	Δv km s^{-1}
CH_2DOH						
89.2512	$2_{0,2}-1_{0,1}\ \mathrm{o}_1$	0.7	17.2	0.19 ± 0.04	0.04	4.3 ± 0.6
89.2754	$2_{0,2}-1_{0,1}\ \mathrm{e}_1$	0.7	13.8	0.16 ± 0.03	0.06	2.6 ± 0.4
89.4079	$2_{0,2}-1_{0,1}\ \mathrm{e}_0$	0.8	4.5	0.31 ± 0.05	0.06	4.7 ± 0.2
110.1054	$9_{1,8}-9_{0,9}\ \mathrm{o}_1$	3.3	83.4	0.42 ± 0.08	0.05	7.4 ± 0.9
133.8473	$3_{0,3}-2_{0,2}\ \mathrm{e}_1$	1.1	18.3	0.60 ± 0.11		
133.8729	$3_{0,3}-2_{0,2}\ \mathrm{o}_1$	1.1	21.7	0.60 ± 0.11		
133.8818	$3_{2,2}-2_{2,1}\ \mathrm{o}_1$	0.6	33.6	0.34 ± 0.07	0.07	4.3 ± 0.9
133.8929	$3_{2,2}-2_{2,1}\ \mathrm{e}_1$	0.6	27.4	0.67 ± 0.14	0.05	12.2 ± 2.2
133.8974	$3_{2,1}-2_{2,0}\ \mathrm{o}_1$	0.6	33.6	0.30 ± 0.07	0.08	3.4 ± 0.6
133.9302	$3_{2,1}-2_{2,0}\ \mathrm{e}_1$	0.6	27.4	0.37 ± 0.15	0.07	4.8 ± 2.2
134.0655	$3_{0,3}-2_{0,2}\ \mathrm{e}_0$	1.2	8.9	0.67 ± 0.33	0.10	6.0 ± 3.3
134.1124	$3_{2,2}-2_{2,1}\ \mathrm{e}_0$	0.7	20.2	0.43 ± 0.15	0.06	6.4 ± 2.3
134.1854	$3_{2,1}-2_{2,0}\ \mathrm{e}_0$	0.7	20.2	0.26 ± 0.06	0.06	4.1 ± 0.8
207.7808	$2_{1,2}-3_{0,3}\ \mathrm{e}_0$	0.3	15.9	1.01 ± 0.25	0.11	8.4 ± 2.5
223.0713	$5_{2,3}-4_{1,4}\ \mathrm{e}_1$	0.6	33.6	1.13 ± 0.42	0.17	6.3 ± 2.5
223.1073	$5_{0,5}-4_{0,4}\ \mathrm{o}_1$	1.8	35.1	0.51 ± 0.18	0.15	3.1 ± 1.2
223.1283	$5_{2,4}-4_{2,3}\ \mathrm{e}_1$	1.4	40.8	0.54 ± 0.26	0.22	2.3 ± 0.7
223.1311	$5_{4,1}-4_{4,0}\ \mathrm{o}_1$	0.6	79.4	0.41 ± 0.16	0.08	4.8 ± 2.1
223.1311	$5_{4,2}-4_{4,1}\ \mathrm{o}_1$	0.6	79.4	0.41 ± 0.16	0.08	4.8 ± 2.1
223.1537	$5_{3,3}-4_{3,2}\ \mathrm{o}_1$	1.0	60.8	0.58 ± 0.09		
223.1537	$5_{3,2}-4_{3,1}\ \mathrm{o}_1$	1.0	60.8	0.58 ± 0.09		
223.3154	$5_{2,3}-4_{2,2}\ \mathrm{e}_1$	1.4	40.8	0.38 ± 0.09	0.16	2.2 ± 0.5
223.4223	$5_{2,4}-4_{2,3}\ \mathrm{e}_0$	1.8	33.6	0.55 ± 0.09	0.10	5.2 ± 0.3
CH_3OD						
110.1889	1_1-1_0	1.6	7.8	0.10 ± 0.02	0.04	2.3 ± 0.5
110.2626	2_1-2_0	2.7	10.8	0.17 ± 0.04	0.03	4.5 ± 1.1
110.4758	3_1-3_0	3.8	15.4	0.30 ± 0.05		
133.9254	$1_{1-}-1_{0+}$	3.2	6.0	0.55 ± 0.18	0.06	8.4 ± 2.8
223.3086	$5_{1+}-4_{1+}$	3.4	26.8	0.09 ± 0.03	0.06	1.4 ± 0.4
226.5387	$5_{0+}-4_{0+}$	3.5	22.7	1.32 ± 0.21	0.23	5.5 ± 0.3
CHD_2OH						
83.1292	$2_0-1_0\ \mathrm{e}_1$	1.4	16.98	0.07 ± 0.02	0.02	3.1 ± 0.7
83.2895	$2_0-1_0\ \mathrm{e}_0$	1.4	4.17	0.09 ± 0.02	0.03	3.2 ± 0.6
83.3036	$2_0-1_0\ \mathrm{o}_1$	1.4	10.33	0.07 ± 0.01	0.03	2.5 ± 0.5
166.234	$4_0-3_0\ \mathrm{e}_1$	2.8	26.69	0.39 ± 0.08		
166.271	$4_{2-}-3_{2-}\ \mathrm{e}_1$	2.1	35.65	0.22 ± 0.07	0.04	5.1 ± 1.8
166.297	$4_{3+}-3_{3-}\ \mathrm{e}_1$	1.2	46.54	0.10 ± 0.08	0.03	3.2 ± 2.2
166.298	$4_{3-}-3_{3-}\ \mathrm{e}_1$	1.2	46.54	0.10 ± 0.08	0.03	3.2 ± 2.2
166.304	$4_{2+}-3_{2+}\ \mathrm{e}_1$	2.1	35.65	0.22 ± 0.06	0.06	3.4 ± 0.9
166.327	$4_0-3_0\ \mathrm{o}_1$	2.8	20.04	0.17 ± 0.10		
166.435	$4_0-3_0\ \mathrm{e}_0$	2.8	13.89	0.48 ± 0.13	0.05	8.7 ± 2.8
207.771	$5_0-4_0\ \mathrm{e}_1$	3.5	33.63	0.44 ± 0.11	0.09	4.4 ± 1.1
207.827	$5_{2-}-4_{2-}\ \mathrm{e}_1$	2.9	42.59	0.19 ± 0.11	0.07	2.5 ± 1.3
207.864	$5_{4-}-4_{4-}\ \mathrm{e}_1$	1.3	68.41	0.43 ± 0.13	0.07	5.6 ± 1.8
207.868	$5_{3-}-4_{3-}\ \mathrm{e}_1$	2.2	53.48	0.17 ± 0.10	0.05	3.4 ± 1.1
207.869	$5_{3+}-4_{3+}\ \mathrm{e}_1$	2.2	53.48	0.17 ± 0.10	0.05	3.4 ± 1.1

Table 2. 10″-averaged column density N(Molecule) and rotational temperature T_{rot} of CH_2DOH, CH_3OD and CHD_2OH respectively. ^{a} Assuming T_{rot} = 47.5 K (see text).

Molecule	N(Molecule) (cm^{-2})	T_{rot} (K)
CH_2DOH	$(3.0 \pm 0.6) \times 10^{15}$	48 ± 3
CH_3OD	$(1.5 \pm 0.7) \times 10^{14}$	20 ± 4
CH_3OD^a	$(2.8 \pm 0.3) \times 10^{14}$	47.5
CHD_2OH	$(6.0 \pm 2.2) \times 10^{14}$	47 ± 7

three molecules are reported in Table 2. The CH_3OD rotational temperature is significatively lower compared with the other two, very probably because the detected lines have lower upper level energies. We therefore estimated the CH_3OD column density assuming the same rotational temperature of the two other species, namely 47.5 K and find the value $(2.8 \pm 0.3) \times 10^{14}$ cm^{-2}. Using the methanol column density derived by van Dishoeck et al. (1995) (3.5×10^{15} cm^{-2} with a source size of 10″), we finally obtain the following fractionation ratios:

$$[CH_2DOH]/[CH_3OH] = 0.9 \pm 0.3$$

$$[CH_3OD]/[CH_3OH] = 0.04 \pm 0.02$$

$$[CHD_2OH]/[CH_3OH] = 0.2 \pm 0.1$$

$$[CH_2DOH]/[CH_3OD] = 20 \pm 14$$

$$[CHD_2OH]/[CH_2DOH] = 0.2 \pm 0.1.$$

If the CH_3OD column density derived with T_{rot} = 47.5 K is taken, the ratios involving this species change by a factor of two, reflecting the increased abundance of this molecule.

4. Discussion and conclusions

Our most dramatic result is the detection in IRAS 16293 of a form of doubly-deuterated methanol along with the detection of both possible singly-deuterated isotopomers of this molecule. Up to now, only a tentative detection of CH_3OD has been reported in a low-mass protostellar source (van Dishoeck et al. 1995). Singly-deuterated methanol has been definitely observed towards Orion (Mauersberger et al. 1988, where $CH_3OD/CH_3OH \sim 0.01$–0.06 and Jacq et al. 1993, where $CH_2DOH/CH_3OH \sim 0.04$) and SgB2 (Gottlieb et al. 1979, with $CH_3OD/CH_3OH \sim 0.01$). Equally strikingly, we find the deuterated forms of methanol to possess a total abundance greater than the main isotopomer in IRAS 16293, even without the contribution of the doubly-deuterated isotopomer CH_2DOD! To date, no other molecule has been observed to show such extreme deuterium fractionation.

As discussed in the Introduction, the abundances of deuterated methanol and deuterated formaldehyde provide a strong test of models involving active grain chemistry. The basic hypothesis behind these models is that formaldehyde and methanol form by the hydrogenation of CO accreted onto the grains via reactions with atomic hydrogen (Tielens & Hagen 1982; Charnley et al. 1997, hereafter CTR97). The enhanced deuteration is caused by an enhanced (atomic) D/H ratio in the gas during the era of mantle formation (Tielens 1983). The hydrogenation and deuteration of CO is predicted to form H_2CO first ($CO \rightarrow HCO \rightarrow H_2CO$) and subsequently CH_3OH ($H_2CO \rightarrow H_3CO \rightarrow CH_3OH$). With some simplifying assumptions, this leads directly to predictions for steady-state ratios of singly- and doubly-deuterated formaldehyde and methanol to their normal isotopic forms in terms of the relative accretion rates of H and D with respect to CO as free parameters (CTR97). The relative accretion rate of H with respect to CO can be derived from the observation of the CO/CH_3OH and H_2CO/CH_3OH abundance ratios. The predictions for the fractionation ratios then depend only on the relative accretion rate of D with respect to CO, or equivalently on the D/H atomic abundance ratio in the accreting gas. Figure 3 shows fractionation ratios predicted by the CTR97 model. In particular, the calculated ratios of singly-deuterated isotopomers to normal species are plotted against the analogous ratios for doubly-deuterated species, both as functions of the D/H atomic ratio in the gas. As seen in the upper panel, the CH_2DOH and CHD_2OH observations are compatible with an atomic D/H ratio of 0.2 in the accreting gas. The CH_3OD abundance falls short of the predicted value for a D/H ratio of 0.2. However, the gas phase abundance of CH_3OD in the hot core can be affected by gas phase ion-molecule reactions. Specifically, protonation of methanol by H_3^+ or H_3O^+ followed by dissociative electron recombination back to methanol will drive the CH_3OD/CH_3OH ratio to the deuterium fractionation of molecules in the warm gas, which is very low (CTR97). The timescale for this process is some 3×10^4 yrs which is comparable to the lifetime of IRAS 16293 ($\sim 2 \times 10^4$, Ceccarelli et al. 2000). We note that this chemical reshuffling of the deuterium will not affect the deuterium fractionation on the methyl group (e.g., CH_2DOH, CHD_2OH). The CTR97 model, however, has some difficulties in explaining the observed formaldehyde fractionation ratios towards IRAS 16293 (Loinard et al. 2000). In particular, the value of atomic D/H compatible with CH_2DOH and CHD_2OH is reasonably compatible with HDCO but results in too low a fractionation ratio for D_2CO by a factor of 5 or so. Possible gas-phase alterations have not been considered. The formaldehyde discrepancy suggests that at least some of the assumptions in the CTR97 model may be too drastic. For example, the CTR97 model contains the approximation that only the accreted H, D and CO are important in the formation of formaldehyde and methanol on the grain surfaces, and that no other reactions compete with formaldehyde and methanol formation.

Very recently, Caselli et al. (2002) (hereafter CSS02) proposed a somewhat more detailed but related model for the formation of formaldehyde, methanol, all of their deuterated isotopomers, and selected other species on grains. In their model, CSS02 consider accretion onto grains of H, D, CO and O, followed by a comprehensive set of reactions to form H_2O, H_2, CO_2, H_2CO, CH_3OH and all singly- and multiply-deuterated isotopomers of these species. Their model differs slightly from that of CTR97 in that it specifically includes small differences in the barriers to reaction between non-deuterated and deuterated species. Yet, in the so-called accretion limit and with the same assumption of rapid diffusion rates, the CSS02 model should yield approximately the same results as the CTR97 model given the same set of chemical reactions and physical conditions. Predictions for methanol and formaldehyde fractionation ratios are indeed similar to the CTR97 model and substantially the same discrepancies remain. In particular, for D/H = 0.3, a temperature of 10 K, and so-called high-density conditions, CSS02 agree approximately with our observed fractionation ratios for CH_2DOH and CHD_2OH, but produce approximately 5 times too much CH_3OD, a value similar to that of CTR97 with D/H = 0.2 and no subsequent gas-phase chemistry. For formaldehyde, CSS02 obtain a fractionation ratio for HDCO that is twice the observed value and a fractionation ratio for D_2CO that is a factor of two below the observed value.

In summary, neither model is in good agreement with all of our data. More importantly perhaps, the CTR97 and CSS02 models require a D/H atomic ratio in the range 0.2–0.3, which is a significantly larger value than can be produced by current gas-phase models, even in the presence of a large CO depletion (e.g. Roberts & Millar 2000a). Future progress will probably require more detailed chemical models in which gas-phase and surface chemistry occur simultaneously. Although such models are currently in existence, they do not yet contain fractionation processes.

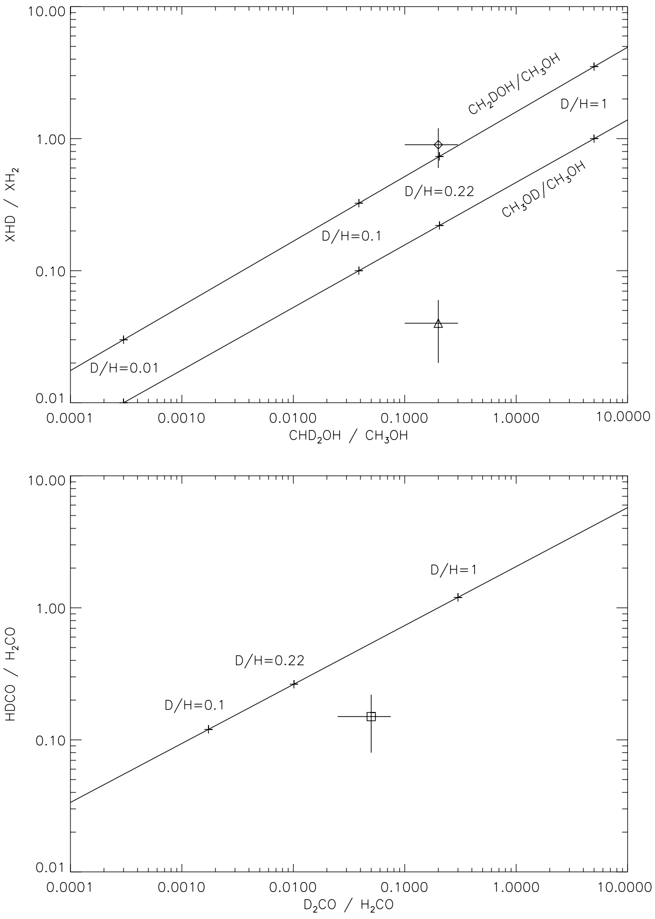

Fig. 3. Model predictions (solid lines, adapted from CTR97) of abundance ratios between singly-deuterated and doubly-deuterated isotopomers with respect to normal species are plotted vs. one another for methanol and formaldehyde. The predictions are obtained as functions of the gas-phase atomic D/H ratio. The observed ratios of Loinard et al. (2000) are also shown. Upper panel: CH_2DOH/CH_3OH (diamond) and CH_3OD/CH_3OH (triangle) versus CHD_2OH/CH_3OH. Lower panel: HDCO/H_2CO versus D_2CO/H_2CO.

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