

# DETECTION OF DEUTERATED FORMALDEHYDE IN INTERSTELLAR CLOUDS

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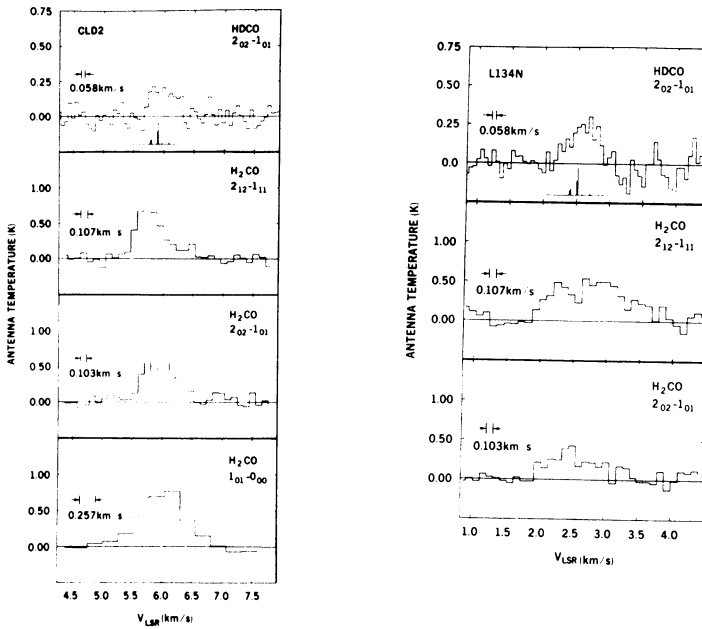
*Deuterated formaldehyde has been detected for the first time in interstellar clouds; the observed ratio HDCO/H<sub>2</sub>CO implies formation by gas phase chemistry.*

Deuterated formaldehyde, HDCO, has been detected for the first time in interstellar clouds from observations of emission from mm radiation in the  $2_{02} \rightarrow 1_{01}$  transition at 128.81291 GHz (Langer, Frerking, Linke, and Wilson 1979 henceforth LFLW). The extent to which deuterium is fractionated can be used as a constraint on the chemistry of formaldehyde in interstellar clouds (Watson, Crutcher, and Dickel 1975). To determine the deuterium enhancement the  $1_{01} \rightarrow 0_{00}$ ,  $2_{02} \rightarrow 1_{01}$ , and  $2_{12} \rightarrow 1_{11}$  transitions of H<sub>2</sub>CO were observed and upper limits were determined for these transitions of the isotope H<sub>2</sub><sup>13</sup>CO. The observed deuterium enhancement strongly suggests that formaldehyde is produced primarily by gas phase ion-molecule reactions rather than on grains.

The observation of HDCO and H<sub>2</sub>CO were made on the Bell Telephone Laboratories 7m antenna in Holmdel, NJ (further details can be found in LFLW). The detections of HDCO and H<sub>2</sub>CO emission in the two dark clouds L134N and Helix Cloud 2 (CLD2) are shown in Figures 1 and 2, respectively (the predicted hyperfine structure is indicated in each figure). For H<sub>2</sub><sup>13</sup>CO our search yielded only upper limits in these sources and the  $1\sigma$  limits on emission are 0.05K for the  $1_{01} \rightarrow 0_{00}$ ,  $2_{01} \rightarrow 2_{01}$ , and  $2_{12} \rightarrow 1_{11}$  transitions in CLD2 and 0.07K for the  $2_{02} \rightarrow 1_{01}$  transition in L134N.

From the shape of the formaldehyde emission spectra observed for L134N and CLD2 it is apparent that these lines are absorbed by low excitation foreground material in the same manner as HCO<sup>+</sup> (Langer et al. 1978) and HNC (Frerking et al. 1979). The mm emission lines of H<sub>2</sub>CO in these clouds must be used cautiously to determine the degree of deuterium enhancement in formaldehyde. Furthermore, the cm absorption lines (Evans et al. 1975) and mm emission lines probably

arise from different regions in these clouds and cannot be used together to determine the physical conditions in the clouds.

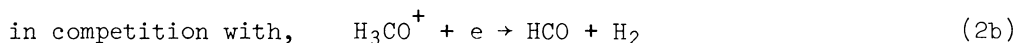


Figures 1 and 2: The observed emission spectra from L134N [RA(1950)=15<sup>h</sup>51<sup>m</sup>30<sup>s</sup>, DEC(1950)=-02°43'30", VLSR=2.5 km/s] and CLD2 [RA(1950)=4<sup>h</sup>38<sup>m</sup>21<sup>s</sup>, DEC(1950)=-25°41'00", VLSR=5.9 km/s], for HDCO and H<sub>2</sub>CO. The velocity resolution is indicated in each figure.

To determine abundances and abundance limits from the measured antenna temperatures an LVG radiative transfer model was used as a guide (cf LFLW). The observed HDCO mm emission from 2<sub>02</sub>→1<sub>01</sub> and the limits set by Angerhofer et al. (1978) on the antenna temperature of the 5cm 1<sub>01</sub>→1<sub>11</sub> line are consistent with hydrogen densities,  $n(\text{H}_2) < 3 \times 10^5 \text{ cm}^{-3}$ . The densities in the regions of L134N and CLD2 where HDCO has been detected have been estimated, from DCO<sup>+</sup> measurements, to be in the range,  $n(\text{H}_2) = 3 \times 10^4$  to  $10^5 \text{ cm}^{-3}$ , (Guelin et al. 1979). Within this range a comparison of HDCO and H<sub>2</sub>CO antenna temperatures yields a ratio HDCO/H<sub>2</sub>CO  $\sim 0.4$ . As has been noted before for DCO<sup>+</sup>/HCO<sup>+</sup> (Langer et al. 1978) self-absorption of H<sub>2</sub>CO emission by low excitation foreground gas can result in an HDCO/H<sub>2</sub>CO intensity ratio which is enhanced with respect to their abundance ratio. To circumvent this difficulty we have determined lower limits on this ratio from our detection limits on H<sub>2</sub><sup>13</sup>CO by adopting a <sup>12</sup>C/<sup>13</sup>C ratio of 60 (Langer et al. 1979). At a density  $n(\text{H}_2) = 3 \times 10^4 \text{ cm}^{-3}$  the ratio HDCO/H<sub>2</sub>CO  $> 0.08$ ; the corresponding deuterium enhancement in HCO<sup>+</sup>, as determined from DCO<sup>+</sup> and H<sup>13</sup>CO<sup>+</sup> measurements, is DCO<sup>+</sup>/HCO<sup>+</sup>  $\approx 0.04$  (Guelin et al 1979). As discussed

below a rate of  $(\text{HDCO}/\text{H}_2\text{CO}) \sim 2(\text{DCO}^+/\text{HCO}^+)$  is consistent with ion-molecule mechanisms for production of formaldehyde.

In interstellar clouds several reactions have been suggested to initiate production of formaldehyde by gas phase chemistry. By one path or another (cf. Prasad and Huntress 1979) these lead to  $\text{CH}_3$  or  $\text{H}_3\text{CO}^+$ . These then produce formaldehyde by the reactions,



In the ion molecule scheme the HDCO is produced by the deuterated form of the same molecules which produce  $\text{H}_2\text{CO}$ , and deuterium enhancement occurs in the precursor ions either through  $\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$  or  $\text{CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$  (cf. Guelin et al 1978). Regardless of which reaction dominates production it can be shown that,

$$(\text{HDCO}/\text{H}_2\text{CO})_{\text{im}} = 2 \frac{\Delta(\text{H}_2\text{CO})}{\Delta(\text{HDCO})} (\text{DCO}^+/\text{HCO}^+) \quad (3)$$

where  $\Delta$  is the destruction rate for each species and where it is assumed that the recombination  $\text{H}_2\text{DCO}^+ + \text{e} \rightarrow \text{HDCO} + \text{H}$  is twice as probable as that to  $\text{H}_2\text{CO} + \text{D}$ , and similarly for  $\text{CH}_2\text{D} + \text{O} \rightarrow \text{HDCO} + \text{H}$  versus  $\rightarrow \text{H}_2\text{CO} + \text{D}$ . The destruction rate  $\Delta = \sum a_i k_i n_i$ , where for each reacting species  $i$ ,  $n$  is the density,  $k$  the reaction rate constant (from Prasad and Huntress 1979) and  $a_i$  a renormalization term to account for destruction processes which lead back to HDCO or  $\text{H}_2\text{CO}$ .

Two possible mechanisms by which grains could play a role in forming HDCO are: 1)  $\text{H}_2\text{CO}$  is produced by the association of atoms on grain surfaces (Watson and Salpeter 1972) and HDCO is formed by ion-molecular reactions, notably by  $\text{H}_2\text{D}^+ + \text{H}_2\text{CO} \rightarrow \text{H}_2\text{DCO}^+ + \text{H}_2$ , (rate constant  $k_4$ ) followed by dissociative recombinations; 2) HDCO comes directly from  $\text{DCO}^+$  reacting at a negatively charged grain surface by  $\text{DCO}^+ + \text{H}_2 + \text{e} \rightarrow \text{HDCO} + \text{H}$  (Watson et al. 1975). In the first case,

$$(\text{HDCO}/\text{H}_2\text{CO})_{\text{g+im}} = \frac{2}{3} \frac{\alpha k_4 \text{H}_3^+}{\Delta(\text{HDCO})} (\text{DCO}^+/\text{HCO}^+) \quad (4)$$

where  $\alpha = k_{2a}/k_{2,\text{tot}}$ , and in the second case,

$$(\text{HDCO}/\text{H}_2\text{CO})_{\text{g+DCO}^+} = \frac{2}{3} \frac{\Delta(\text{H}_2\text{CO})}{\Delta(\text{HDCO})} (\text{DCO}^+/\text{HCO}^+) \quad (5)$$

assuming the  $\text{DCO}^+$  reaction on the grain leads to HDCO twice as often as  $\text{H}_2\text{CO}$ .

The major uncertainty in evaluating the deuterium enhancement is the relative efficiency with which  $\text{H}_3\text{CO}^+$  and  $\text{H}_2\text{DCO}^+$  recombine to produce  $\text{H}_2\text{CO}$  and  $\text{HDCO}$  rather than other products (Eq. 2b and 2c). While laboratory data for the total recombination rate constant for deuterated and non-deuterated ions are similar (Mul and McGowan 1979), there are no measurements of branching ratios. Theoretical calculations by Herbst (1978) suggest that it is unlikely that only one hydrogen will be ejected. We adopt an equal branching ratio for all likely products (Prasad and Huntress 1979) corresponding to  $\alpha = 1/3$ . For this choice it can be shown, in general, that for ion-molecule production  $\text{HDCO}/\text{H}_2\text{CO} \approx 2 (\text{DCO}^+/\text{HCO}^+)$ . For production via  $\text{DCO}^+$  on grains the ratio is  $\sim 2/3 (\text{DCO}^+/\text{HCO}^+)$  and for the combined grain plus ion-molecule scheme (the first grain mechanism) the ratio is  $< 1/3 (\text{DCO}^+/\text{HCO}^+)$  and, when estimates of  $\text{H}_3^+$  and the other ion abundances are included, it is closer to  $1/10 (\text{DCO}^+/\text{HCO}^+)$ .

Our observations of  $\text{HDCO}$  indicate that  $(\text{HDCO}/\text{H}_2\text{CO}) \sim 2(\text{DCO}^+/\text{HCO}^+)$  which strongly suggests that formaldehyde is produced primarily by ion-molecule reactions. Laboratory measurements of the branching ratios for dissociative recombination of  $\text{H}_3\text{CO}^+$  and  $\text{H}_2\text{DCO}^+$  are needed to be certain that grains do not play some role.

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#### DISCUSSION FOLLOWING LANGER

*Allamandola:* You argue that  $\text{HCO}^+/\text{DCO}^+$  is more consistent with ion-molecule reactions in the gas-phase than with interactions with grains. Would you expect similar behavior for  $\text{HCO}/\text{DCO}$  neutral? Have any such observations been made? Since this molecule is easily made by neutral species combining in the grain, this may be an important test.

*Langer:* Observations of DCO and HCO could conceivably discriminate between the different production mechanisms.

*Winnewisser:* I want to congratulate you on finding interstellar HDCO. The transition you have used is the one we measured several years back when I was at the National Research Council. However the frequency accuracy was at best  $\pm 150$  kHz, so the velocity determination may be in error. How closely do the velocities agree with those of other molecules in TMC1?

*Langer:* The HDCO peak velocity agrees with that of  $\text{H}^{13}\text{CO}^+$  to within 0.1 km/s, and suggests an uncertainty in frequency of  $\sim 80$  kHz, of which half is due to the uncertainty in the determination of the  $\text{H}^{13}\text{CO}^+$  frequency.

*W. Watson:* If the laboratory rate for  $\text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + \text{h}\nu$  is as rapid as suggested by the laboratory people, the channel  $\text{CH}_3^+ + \text{HD} \rightleftharpoons \text{CH}_2\text{D}^+ + \text{H}_2$  for fractionation would appear to be much less important than previously thought. Would this affect your analysis?

*Langer:* It conceivably could if the rate constant were  $\gg 10^{-13} \text{cm}^3 \text{s}^{-1}$  and if the  $\text{CH}_2\text{D}^+$  were formed only by the reaction  $\text{CH}_3^+ + \text{HD}$ . If deuterium fractionation proceeds primarily through  $\text{H}_3^+ + \text{HD}$ , however, then the analysis will not be affected.

*Fukui:* Watson et al. (1975) obtained an upper limit for HDCO which is significantly smaller than your detection. Could you explain the discrepancy?

*Langer:* Their search was for the 5 cm line of HDCO, and the interpretation of column density is very sensitive to collision rates and temperature. Recent excitation calculations show that their limits are consistent with the mm emission.