A&A 381, L17–L20 (2002)
DOI: 10.1051/0004-6361:20011547

Astronomy
&
Astrophysics

The puzzling detection of D_2CO in the molecular cloud L1689N

C. Ceccarelli[1], C. Vastel[2], A. G. G. M. Tielens[3], A. Castets[1], A. C. A. Boogert[4], L. Loinard[5], and E. Caux[2]

[1] Observatoire de Bordeaux, BP 89, 33270 Floirac, France
[2] CESR CNRS-UPS, BP 4346, 31028 Toulouse Cedex 04, France
[3] SRON, PO Box 800, 9700 AV Groningen, The Netherlands
[4] California Institute of Technology, Downs Laboratory of Physics 320-47, Pasadena, CA 91125, USA
[5] Instituto de Astronomía, UNAM, Apdo Postal 72-3 (Xangari), 58089 Morelia, Michoacán, México

Received 11 October 2001 / Accepted 8 November 2001

Abstract. We present new observations of the D_2CO emission towards the small cloud L1689N in the ρ Ophiuchus complex. We surveyed five positions, three being a cut across a shock site and two probing the quiescent gas of the molecular cloud. We detected D_2CO emission in the first three positions. The measured $[D_2CO]/[H_2CO]$ is about 3%, whereas it is $\leq$2% in the quiescent gas. We discuss the implications of these new observations, which suggest that the bulk of the D_2CO molecules is stored in grain mantles, and removed from the cold storage by the shock at the interface between the outflowing and quiescent gas. We review the predictions of the published models proposed to explain the observed high deuteration of formaldehyde. They fall in two basic schemes: gas phase and grain surface chemistry. None of the reviewed models is able to account for the observed $[D_2CO]/[H_2CO]$ abundance ratio. A common characteristics shared by the models is apparently that all underestimate the atomic [D]/[H] ratio in the accreting gas.

Key words. ISM: abundances – ISM: molecules – stars: formation – ISM: individual: L1689N

1. Introduction

The study of doubly deuterated molecules in the interstellar medium has been booming in the last few years, since the discovery of an extremely large amount, ~10% of doubly deuterated formaldehyde in the low mass protostar IRAS 16293-2422 (Ceccarelli et al. 1998), a fractionation about 25 times larger than in Orion (Turner 1990). This value, compared with the abundance of the deuterium in the solar neighborhood (1.5×10^{-5}; Linsky 1998), gives an enhancement of the formaldehyde fractionation in IRAS 16293-2422 over eight orders of magnitude! This first discovery has been followed by other studies, which better measured and confirmed this very large degree of deuteration in IRAS 16293-2422 (Loinard et al. 2000), and studied its spatial distribution (Ceccarelli et al. 2001). Similar large amounts of doubly deuterated formaldehyde (D_2CO) as well as ammonia (ND_2H), have successively been observed towards another very young protostar, 16293E, which lies in the same molecular cloud, L1689N, as IRAS 16293-2422 (Loinard et al. 2001). And, finally, preliminary results of an on going project show that very likely *all* low mass protostars contain similar large fractions of doubly deuterated formaldehyde with respect to H_2CO, whereas high mass protostars do not (Loinard et al. in preparation; Ceccarelli 2001). The ensemble of these observations suggests that such a large deuteration is obtained during the cold and dense pre-collapse phase of the low mass protostars: highly deuterated ices are very likely formed via active grain chemistry (Tielens 1983), stored onto the grain mantles and eventually released in the gas phase during the collapse, when the heating of the newly formed protostars evaporate the ices (Ceccarelli et al. 2001). Two key points of this picture are:

a) the mantle ices formed in the pre-collapse phase contain the bulk of the doubly deuterated formaldehyde observed now in the gas phase;

b) the high degree of deuteration is obtained when the gas is cold ($\leq$20 K). In fact a large degree of deuteration requires either the enhancement of the atomic [D]/[H] ratio of the gas accreting into the mantles, if active grain chemistry is at the origin of the deuteration (Tielens 1983), or the enhancement of the $[H_2D^+]/[H_3^+]$ ratio, if the deuteration occurs in the accreting gas (Roberts & Millar 2000a). Either way, low temperatures, as those expected during the pre-collapse phase (e.g. Zucconi et al. 2001), are necessary for the enhancement to occur. Incidently, this might explain why massive protostars have a much lower degree of deuteration, as on average they go through

---

Send offprint requests to: C. Ceccarelli,
e-mail: `ceccarel@observ.u-bordeaux.fr`

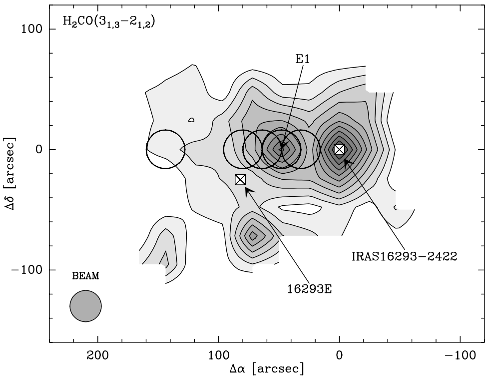

Fig. 1. The five positions observed in the D_2CO line, superimposed to the H_2CO map by CCL2001. The two sources in the region are marked, as well as the shocked gas site E1. The $(0'', 0'')$ position corresponds to $\alpha(2000) = 16^h32^m22.6^s$, $\delta(2000) = -24°28'33''$.

a warmer pre-collapse phase (Ceccarelli et al. 1998; Loinard et al. 2000), although other explanations are certainly possible. From all this it follows that the mantle composition of high and low mass protostars may differ, as also suggested by other recent observations (Ceccarelli et al. 2000). Although the described picture is consistent with all the observations so far available towards protostars, the very origin of the deuteration, whether via active grain chemistry or gas phase formation is still widely debated (see for example Roberts & Millar 2000b). The reason is first the relatively small body of available observations and second the discovery that at least in one dark molecular cloud, L134N, ammonia shows also relatively large deuteration, namely $[NHD_2]/[NH_3] \sim 0.1\%$ (Roueff et al. 2000). Specifically, the L134N observations are well accounted for by gas phase models, which predict large $[NHD_2]/[NH_3]$ ratios when CO is depleted (Roberts & Millar 2000b; Rodgers & Charnley 2001). The same models predict also large doubly deuterated formaldehyde abundances, given a large enough (a factor ~30) CO depletion (Roberts & Millar 2000a,b).

In order to enlarge the observational framework to a molecular cloud, to compare it with model predictions and to stimulate further modeling, we searched for D_2CO emission in the cloud, L1689N, harboring the first two protostars in which D_2CO was detected, namely IRAS 16293-2422 and 16293E (Castets et al. 2001; herein after CCL2001). This molecular cloud belongs to the ρ Ophiuchus complex at 120 pc (Knude & Hog 1998).

2. Observations and results

We obtained a cut of the D_2CO $4_{0,4}$–$3_{0,3}$ (at 231.410 GHz) and a map of H_2CO $3_{1,3}$–$2_{1,2}$ (at 211.211 GHz) emission across L1689N, using the CSO and SEST telescopes respectively. The H_2CO observations have been previously reported in CCL2001. The CSO observations were obtained in July and September 2001 with the 230 GHz receiver; the telescope main beam efficiency $\eta_{\rm MB}$ and the beamwidth at this frequency are 0.70 and 32″ respectively (see the WEB site at `http://www.submm.caltech.edu/cso/`). Pointing and focus were checked regularly on Mars. The pointing accuracy was found to be better than 3″. System temperature was typically $T_{\rm sys} \sim 350$ K during the observations. The observations were made in position switching mode with an OFF position offset equal to $(-180'', 0'')$. The integration times at each position are ~15 min in the H_2CO brightest points and ~60 min in the weakest ones. The spectra were analyzed with an acousto-optical spectrometers (AOS) with a total bandwidth of 50 MHz and an effective spectral resolution of 50 kHz, equivalent to 0.06 km s^{-1}. Hanning smoothing was applied to each spectrum yielding a velocity resolution of 0.126 km s^{-1}.

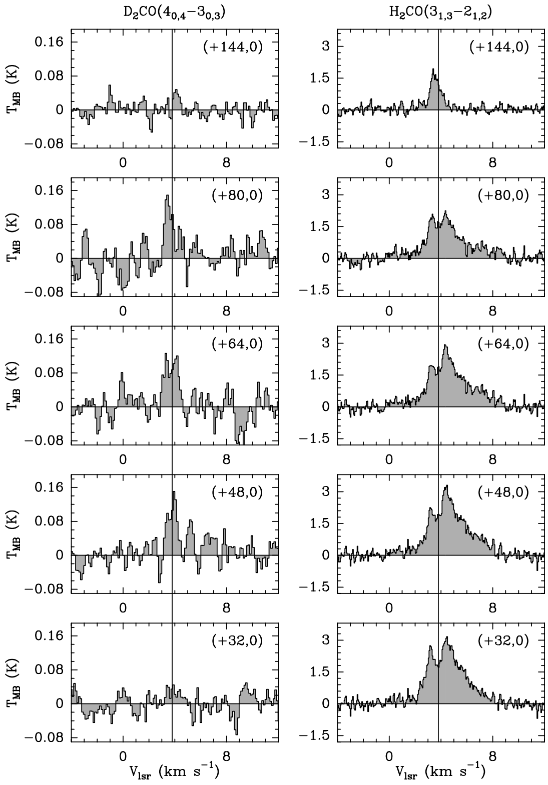

Fig. 2. D_2CO $4_{0,4}$–$3_{0,3}$ and H_2CO $3_{1,3}$–$2_{1,2}$ (smoothed to the CSO beam) line spectra at the five observed positions. The temperature is the main beam temperature $T_{\rm mb}$.

Figure 1 shows the five positions in which we searched for D_2CO emission, superimposed to the H_2CO map (CCL2001). Four positions are a linear cut, spaced by 16″, starting from the border of the envelope of IRAS 16293, and the last position is far from any H_2CO emission peak. Figure 2 shows the D_2CO and H_2CO (smoothed to the CSO resolution) spectra at the five observed positions. As extensively discussed in CCL2001, relatively bright H_2CO emission is associated with the entire cloud, with a few peaks coinciding with the shocks at the interface between the outflows emanating from the protostars in L1689N and the cloud material. From Figs. 1 and 2 it is clear that our D_2CO cut encompasses one shock, named E1 in CCL2001, whereas the last point at $(144'', 0'')$ picks up quiescent material belonging to the cloud. D_2CO is definitively detected in the three positions encompassing the shock site E1, whereas we only obtained upper limits to the D_2CO emission in the other two positions. The D_2CO lines seem to be slightly narrower than the H_2CO ones, but the reached sensitivity is not enough to firmly establish it. Note that the dip around the systemic velocity in the H_2CO lines is probably foreground absorption from the quiescent cloud, as thoroughly discussed in Loinard et al. (2000). The derived D_2CO and H_2CO column densities at each position, as well as the $[D_2CO]/[H_2CO]$ abundance ratios are reported in Table 1, assuming that the H_2CO and D_2CO lines are both optically thin and using $T_{\rm ex} = 9$ K. The H_2CO column density has been computed by integrating the line between -5 and $+15$ km s^{-1}. Note that although the values of the column densities depend on the assumed excitation temperature, the $[D_2CO]/[H_2CO]$ abundance ratio does not. This is because the two observed lines have similar upper level energies and spontaneous emission coefficients, and the two molecules have a similar structure and therefore have similar excitation conditions. In this respect thus, the ratio of the two observed line intensities is a straightforward measurement of the $[D_2CO]/[H_2CO]$ abundance ratio. The largest uncertainty arises from the H_2CO line opacity. Yet, based on previous observations of H_2CO line opacities in molecular clouds we expect only a moderate opacity (Dickens & Irvine 1999). This expectation is also supported by our own measurement of the opacity of the H_2CO $3_{1,3}$–$2_{1,2}$ line in the direction of IRAS 16293–2422, as the beam of these observations encompasses the cloud emission too (Loinard et al. 2000). Given the uncertainty on the H_2CO line opacity (which can easily be a factor two), however, the reported $[D_2CO]/[H_2CO]$ abundance ratio has strictly to be considered as an upper limit to the true value. Yet, the actual value is unlikely to differ from that reported here by more than a factor two.

3. Discussion and conclusions

Two remarkable results of these observations are:
a) the measured relatively large $[D_2CO]/[H_2CO]$ abundance ratio, $\sim$3%, in the positions encompassing the shocked site E1, and
b) the lack of detected D_2CO emission in the positions which probe the quiescent gas of the cloud.

Together with the observation that H_2CO abundance is enhanced in E1 (see CCL2001 for a detailed discussion), points a) and b) suggest that the D_2CO emission that we see in the gas phase is not a present day gas phase product, but it is likely the result of the desorption of the grain mantles caused by the shock in E1. Note that the relatively narrow D_2CO lines may reflect deuterium re-distribution in the shocked and warmest gas probed by the high velocity wings. Intuitively, the relatively large temperature would affect more the deuterated molecules D_2CO, very sensitive to the gas temperature, with respect to H_2CO, but detailed modeling is necessary to confirm this suggestion. We have therefore evidence that most, if not all, of the D_2CO is stored in the ice mantles, either directly accumulated from the accreting gas, or formed on the grain surfaces through reactions between accreted species. Once again, the obvious question to answer is: what of the two proposed schemes, accreted gas versus grain surface formation, is correct? Note that, since we are far away from the protostars and their envelopes, and from any condensation, there is no reason to claim that in a previous phase the same region was colder and denser. Hence, if the deuteration originates in the accreted material, it has to be explained for cloud conditions similar to those presently observed. Unfortunately, the upper limits we obtain in the quiescent gas ($\leq$2%) cannot definitively exclude that the cloud gas (i.e. the accreting material) is as well enriched in D_2CO, given the uncertainty that we have on the opacity of the H_2CO line. However, theoretical arguments help enlighting this point. Recent modeling of gas phase chemistry shows that large fractions of D_2CO over H_2CO are obtained when the gas is very depleted of molecules and atoms (Roberts & Millar 2000a,b). Specifically, the Roberts & Millar (2000b) model predicts that $[D_2CO]/[H_2CO] \sim 3\%$, i.e. our observed value, when the CO abundance drops by about a factor 30. Caux et al. (1999) showed that the atomic oxygen abundance is $\sim$50 times larger than CO in L1689N, implying a CO depletion by about a factor 25, which would agree with the Roberts & Millar model predictions. However, in the same model atomic oxygen would have to be depleted as well by about the same amount than the CO. The very reason is that both CO and O efficiently destroy H_3^+, with O being just a mere factor 2.5 less efficient than the CO (according the UMIST database at `http://www.rate99.co.uk/`). When CO and O are depleted, H_3^+ is destroyed by the reaction with HD, producing H_2D^+; consequently, an enhanced $[H_2D^+]/[H_3^+]$ ratio is obtained, which propagates the deuterium to other molecules at temperatures lower than 30 K (Roberts & Millar 2000a). Therefore both CO and O have to be depleted to give a large deuteration in the gas phase, and this is certainly not the case for L1689N. We are hence forced to conclude that present gas phase schemes are unable to account for the observed $[D_2CO]/[H_2CO]$ ratio.

Table 1. Computed D_2CO and H_2CO column densities and $[D_2CO]/[H_2CO]$ abundance ratios in the five observed positions. The upper limits are 1σ and are computed assuming a linewidth equal to 2 km s^{-1}. The errors are the statistical errors only.

Position α, δ	N(D_2CO) [10^{12} cm^{-2}]	N(H_2CO) [10^{12} cm^{-2}]	$[D_2CO]$ / $[H_2CO]$
32, 0	$\leq$0.7	52 ± 6	$\leq$0.01
48, 0	2.2 ± 0.3	78 ± 7	0.03 ± 0.02
64, 0	2.0 ± 0.3	65 ± 7	0.03 ± 0.02
80, 0	1.1 ± 0.3	39 ± 7	0.03 ± 0.02
144, 0	$\leq$0.4	20 ± 6	$\leq$0.02

As already noticed in previous works dealing with the large D_2CO abundance, active grain chemistry seems to offer a natural explanation (see the Introduction). Tielens (1983) was the first to predict that formaldehyde deuteration can be largely enhanced by surface chemistry, thanks to hydrogen abstraction and deuterium addition reactions at the grain surface. His numerical model predicted $[D_2CO]/[H_2CO] \sim 5\%$ for cloud densities $\sim 10^5$ cm^{-3}, which are remarkably in agreement with the density ($\sim 10^5$ cm^{-3}; Caux et al. 1999) in L1689N. However, since that pioneer work, some key reactions in the deuteration network have been revised, lowering by a large factor the atomic [D]/[H] ratio (about equal to $[H_2D^+]/[H_3^+]$) in the accreting material, which in Tielens's model was ~ 1 at 10^5 cm^{-3} (his Fig. 1a). More recent gas phase models now predict $[D]/[H] \sim 0.01$ unless the gas is very depleted by CO and O molecules (Roberts & Millar 2000a; Herbst et al. 2001). Consequently, it is possible that the Tielens's model may overestimate the $[D_2CO]/[H_2CO]$ ratio. More recent calculations of the H_2CO deuteration via grain-surface chemistry has been presented by Charnley et al. (1997). In this paper the authors used a different approach: a simplified scheme in which they only considered addition reactions and ignored all other reactions. The present observations can put some constraints on this theory too. If the surface hydrogenation and deuteration of CO follows the simple scheme by Charnley, Tielens & Rodgers (see their Fig. 1), namely if CO hydrogenation and deuteration are the main routes to the formation of H_2CO and D_2CO respectively on the grain surfaces, then it is possible to demonstrate that the $[D_2CO]/[H_2CO]$ ratio is equal, within 30%, to $0.1 \times ([D]/[H])^2$ in the accreting gas for their choice of the reaction barriers involved. The $[D_2CO]/[H_2CO]$ value (~ 0.03) observed towards L1689N would imply then $[D]/[H] \sim 0.5$ in the accreting gas. This seems to be a rather large ratio with respect to the predictions of gas phase models (see above), and not supported by previous observations of the $[DCO^+]/[HCO^+]$ ratio, ~ 0.01 (van Dishoeck et al. 1995), which is predicted to be of the same order of the [D]/[H] ratio. Although this measure does not really refer to the cloud but rather to the envelope of IRAS 16293–2422, the beam used for obtaining it encompasses the cloud, so the $[DCO^+]/[HCO^+]$ in the cloud is not likely to be very different. We hence conclude that most probably the simple scheme by Charnley et al. (1997) is not enough to explain our observations, and that other routes of grain-surface formation, specifically abstraction reactions, may be involved. Finally, very recently Herbst et al. (2001) presented the results of their model of deuteration via grain surface chemistry, which uses a different approach ("reaction limit" approximation) than the Tielens's and collaborators one ("accretion limit" approximation). Basically, Herbst, Caselli & Shalabeia included a full network of reactions on the grain surfaces in the so called "reaction limit" approximation, which is known to have a theoretical validity problem. In their work, however, Herbst, Caselli & Shalabeia included a correction to the used reactions in order to reproduce the theoretically more exact "accretion limit" models in the limit of interstellar clouds conditions (Caselli et al. 1998). As in the case of the above discussed models, Herbst, Caselli & Shalabeia model fails to reproduce the large formaldehyde deuteration which we observe in L1689N. Once again, the very difficulty is that to obtain large $[D_2CO]/[H_2CO]$ ratios, corresponding large [D]/[H] ratios are required.

In conclusion, all the present models, whether gas phase or grain surface, have difficulty to account for our $[D_2CO]/[H_2CO]$ measurement. The bottom line is that all the reviewed models require large atomic [D]/[H] ($\sim [H_2D^+]/[H_3^+]$) ratios in the gas phase to reach the large observed $[D_2CO]/[H_2CO]$ ratio. Therefore they all share the same basic problem of underestimating the gas phase atomic [D]/[H] abundance ratio in molecular cloud conditions. We finally remark that the $[D_2CO]/[H_2CO]$ ratio that we find in the desorbed mantles around E1, 3%, is similar to what found at the border of the envelope surrounding IRAS 16293–2422, and less than the value found in the envelope itself, where it reaches 16% (Ceccarelli et al. 2001), or the value measured towards 16293E, $40 \pm 20\%$ (Loinard et al. 2001). This tell us that, as suspected, deuteration of formaldehyde is more efficient in the cold and dense collapse or pre-collapse phase leading to the formation of the protostar.

Acknowledgements. We wish to thank Paola Caselli and Tom Millar for fruitful discussions on the deuteration in their chemical models. The Caltech Submillimeter Observatory is funded by the NSF through contract AST-9980846.

References

Caux, E., Ceccarelli, C., Castets, A., et al. 1999, A&A, 347, L1
Caselli, P., Hasegawa, T. I., & Herbst, E. 1998, ApJ, 495, 309
Castets, A., Ceccarelli, C., Loinard, L., Caux, E., & Lefloch, B. 2001, A&A, 375, 40 (CCL2001)
Ceccarelli, C., Castets, A., Loinard, L., Caux, E., & Tielens, A. G. G. M. 1998, A&A, 338, L43
Ceccarelli, C., Loinard, L., Castets, A., Faure, A., & Lefloch, B. 2000, A&A, 362, 1122
Ceccarelli, C., Loinard, L., Castets, A., et al. 2001, A&A, 372, 998
Ceccarelli, C. 2001, in Proc. Deuterium in the Universe, ed. Roueff & Gerin
Dickens, J. E., & Irvine, W. M. 1999, ApJ, 518, 733
Herbst, E., Caselli, P., & Shalabeia, S. 2001, in Proc. Deuterium in the Universe, ed. Roueff & Gerin
Knude, J., & Hog, E. 1998, A&A, 338, 897
Linsky, J. L. 1998, Space Sci. Rev., 84, 285
Loinard, L., Castets, A., Ceccarelli, C., et al. 2000, A&A, 359, 1169
Loinard, L., Castets, A., Ceccarelli, C., Caux, E., & Tielens, A. G. G. M. 2001, ApJ, 552, L163
Roberts, H., & Millar, T. J. 2000a, A&A, 361, 388
Roberts, H., & Millar, T. J. 2000b, A&A, 364, 780
Rodgers, S. D., & Charnley, S. B. 2001, ApJ, 553, 613
Roueff, E., Tiné, S., Coudert, L. H., et al. 2000, A&A, 354, L63
Roueff, E., Tiné, S., Coudert, L. H., et al. 2001, ApJ, 554, 734
Tielens, A. G. G. M. 1983, A&A, 119, 177
Turner, B. E. 1990, ApJ, 362, L29
Zucconi, A., Walmsley, M., & Galli, D. 2001, A&A, 376, 650