DEUTERATED MOLECULES IN INTERSTELLAR CLOUDS

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ABSTRACT. We show that deuteration in DCN and HDCO probably derives from CH_2D^+ in warm clouds, and that the levels of deuteration observed in those clouds require that radiative association play an important role in the chemistry of interstellar clouds.

1. THE OBSERVED DEUTERATED MOLECULES

The study of isotopic abundance variations in a variety of locales forms an important branch of astrochemistry. Of the observed isotopes, deuterium occupies a prominent niche: it is the most abundant scarce isotope of all the isotopic forms of the elements. The astral creation of fragile deuterium atoms poses stimulating problems for astrophysicists--the existing reservoir is thought to be primordial. The large relative mass difference between hydrogen and deuterium underlies different chemical sensitivities in the two species. A particularly fortunate result of this is that deuterium becomes heavily fractionated in cold clouds, its abundance relative to hydrogen climbing as much as three orders of magnitude. Thus, abundant molecules with isotopically substituted deuterium atoms are not difficult to observe. A modest collection of observations of several isotopic forms of a molecule affords a unique test of its astrochemistry.

Deuterium-substituted forms of twelve molecules have been observed, among which twenty-eight transitions have been studied. There are important newcomers to this list, chief among them H_2D^+ (Phillips et al. 1985). Another very interesting recent detection is that of C_2D (Combes et al. 1985, Vrtilek et al. 1985).

By far the most discerning scrutiny has been lavished on DCO^+, at least partially because of its strength (reaching 5K) in a number of clouds. Surveys of DNC and DCN have also been made and a handful of observations are available for HDCO, N_2D^+ and HDO. Watson (1974, 1976) predicted that fractionation of deuterium would be strongest in cold dark clouds. The surveys of a number of clouds of varying temperatures have corroborated this expectation and revealed some interesting

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differences in the behavior of deuterated molecules. Watson's theory has recently been expanded by Dalgarno and Lepp (1984) to include reactions involving atomic deuterium.

Snell and Wootten (1979) found the DNC/HNC abundance ratio to be strongly temperature dependent. Only scanty $HN^{13}C$ data was presented, however, and effects of scattering and absorption in the HNC line may blemish their analysis.

A more complete set of data was presented by Wootten, Loren and Snell (1982) and by Guelin, Langer and Wilson (1982) for several isotopes and transitions of DCO^+. This data provided irrefutable evidence for a remarkable temperature dependence for the extent of deuterium fractionation. Interestingly, though, DCO^+ has not been unambiguously detected in the warmest and usually most productive astrochemical hunting ground, OMC1 (Penzias 1979). This is curious, as DCN, DNC and some other heavily deuterated molecules can have quite strong emission in OMC1. Apparently, DCO^+ is depleted in warmer clouds when compared to the colder ones, while DCN shows a smaller temperature effect.

2. DEUTERIUM CHEMISTRY IN INTERSTELLAR CLOUDS

2.1. Basic Reactions

The mechanism which Watson (1974) proposed for the observed degree of enhancement of deuterium in interstellar molecules commences with an exchange reaction of the type

$$AX_n^+ + HD \Longleftrightarrow AX_{n-1}D^+ + H_2 + dE \quad (1)$$

where dE is the zero point vibrational energy difference between the products and the reactants.

Important examples of this type of reaction in dense regions are

$$H_3^+ + HD \Longleftrightarrow H_2D^+ + H_2 + dE_1, \quad (2)$$

$$CH_3^+ + HD \Longleftrightarrow CH_2D^+ + H_2 + dE_2 \quad (3)$$

where $dE_1/k \sim 150K$ (Adams and Smith 1981; see discussion therein) and $dE_2/k \sim 370K$ (Smith, Adams and Alge 1982).

Recently, Croswell and Dalgarno (1984) suggested that enough atomic deuterium may be present in clouds of low to moderate density that ion-atom reactions could dominate (2), (3) and (4) in the production of fractionated molecules. Dalgarno and Lepp (1984) presented a revised theory of the fractionation of interstellar deuterium which takes into account atomic processes as well as the newly measured slow electron recombination rate of H_3^+ (Smith and Adams 1984). In this view, atomic deuterium is enhanced relative to atomic hydrogen because the primary deuterium source is electron recombination onto DCO^+, which is highly enhanced relative to HCO^+. However, Tielens (1983) noted that atomic deuterium is preferentially depleted onto grains, and therefore the atomic [D]/[H] ratio may not be well determined. Dalgarno and Lepp estimate that these atomic deuterium reactions could account for between 20% and 50% of the fractionation seen in DCO^+. Reaction rates for the relevant reactions were measured by Adams and Smith (1985), and they corroborate this view.

Reactions (2) and (3) may play a role in fractionation of HCO^+, HCN or H_2CO, e.g.,

Route (2)

HCO^+:
$$H_2D^+ + CO \longrightarrow HCO^+ + HD$$
$$\longrightarrow DCO^+ + H_2.$$

HCN:
$$H_2D^+ + HCN \longrightarrow HCNH^+ + HD$$
$$\longrightarrow DCNH^+ + H_2,$$

followed by electron recombination.

H_2CO:
$$H_2D^+ + H_2CO \longrightarrow H_3CO^+ + HD$$
$$\longrightarrow H_2DCO^+ + H_2,$$

followed by electron recombination.

Route (3)

HCO^+:
$$CH_2D^+ + O \longrightarrow HCO^+ + HD$$
$$\longrightarrow DCO^+ + H_2.$$

HCN:
$$CH_2D^+ + N \longrightarrow HCNH^+ + HD$$
$$\longrightarrow DCNH^+ + H_2,$$

followed by electron recombination.

H_2CO:
$$CH_4D^+ + e \longrightarrow CH_2D + H_2$$
$$CH_2D + O \longrightarrow HDCO + H.$$

2.2. The Evidence for the Role of Reaction (2)

Note that among the observed deuterated molecules, N_2D^+ cannot be produced by reaction (3). Its abundance therefore reflects the importance of reaction (2), or of deuteration through ion-atom reactions. Much evidence points to reaction (2) dominating deuterium fractionation in the coldest clouds:

(1) In TMC1 the abundance ratios R_{AB} (R_{AB}=[DAB]/[HAB]) are $R_{CO^+} \sim R_{N2^+} \sim R_{NC} \sim R_{C5N} \sim R_{C3N} \leq R_{CN} \leq R_{HCO}$ (Guelin *et al*. 1982, Wootten and Greason 1985, Schloerb *et al*. 1981, Langer *et al*. 1979, Langer *et al*. 1980 and MacLeod, Avery and Broten 1980, Suzuki, this conference). The only clearly discordant observation in this group is that of the DC_3N/HC_3N ratio, and its high value has been plausibly explained by a higher than assumed optical depth in the HC_3N line, demonstrated by the ^{13}C observations reported by Suzuki (this conference). Reaction (2) is

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therefore sufficient to account for deuteration in TMC1 within the uncertainties.

(2) The value of $R_{N_2^+}$ in TMC1 requires operation of reaction (2), as the only other route of deuteration is via an atomic exchange, unlikely in a dark cloud possessing no internal source capable of dissociating molecules into atoms.

(3) Phillips et al. (1985) have provided apparent observational confirmation of the presence of interstellar H_2D^+ in NGC2264. The single detected line could be confirmed through observation of a strong temperature dependence in the H_2D^+ abundance in a variety of sources, as seen in DCO^+. The 1_{10}->1_{11} transition detected lies between the ground and first excited state of orth-H_2D^+ at about 100K above the ground state of the molecule. To derive an abundance estimate from the observation, an assumption must be made about the distribution of molecules between ortho and para states. Phillips et al. (1985) found that the line strength was consistent with partial thermalization of H_2D^+ between its para and ortho states in NGC2264, and probably also in TMC1. Because of the higher energy of the ortho-H_2D^+ ground state, this puts detection of the 1_{10}->1_{11} transition at a disadvantage, as the relative population in these states is smaller. Furthermore, the transition lies in a frequency range which is extremely difficult to observe with ground-based telescopes.

(4) The observed temperature dependence of the DCO^+/HCO^+ ratio follows extremely well that expected if the deuteration ultimately derives from H_2D^+ (Wootten, Loren and Snell 1982, Herbst 1982). Note that this is unchanged by contributions from atomic D, as its ultimate source is from electron recombination of DCO^+.

2.3. The Evidence for the Role of Reaction (3)

Straightforward chemical considerations lead to the conclusion that simultaneous operation of routes (2) and (3) lead to quite similar fractionation extents at small temperatures, but at large temperatures this is not true. The archetypical high temperature (T_k~75K) source is OMC1, and its pattern of deuteration is distinctly different from those in the dark cloud TMC1 (T_k~10K).

(1) Comparing the extent of fractionation in DCN and DCO^+, we see that DCN fractionation has reached similar levels in TMC1 as has DCO^+, while in OMC1 the level of deuteration in DCN far exceeds that in DCO^+, for which but a single 3 sigma observation has been reported. To be specific, the abundance ratio is $R_{CO+}<0.002\pm0.0008$ (Penzias 1979) in OMC1 while in the cold dark cloud TMC1 it is $R_{CO+}=0.015\pm0.002$ (Guelin et al. 1982). Note that R_{CO+} shows half an order of magnitude of difference between the clouds. This behavior is in accord with the view that DCO^+ is formed overwhelmingly from H_2D^+ under a range of astrophysical circumstances.

(2) Deuteration of formaldehyde appears quite similar in the two sources, with R_{HCO}=0.01->0.03 (Loren and Wootten 1985) in OMC1 and $R_{HCO}<0.01$ (Langer et al. 1979) in TMC1. Loren and Wootten (1985) propose that this observation argues for deuterium enhancement in CH_3^+, and an important role for reaction (3) in H_2CO chemistry, a logical

choice as the CH_3 + O reaction has long been thought to dominate H_2CO production.

(3) Further evidence for the importance of CH_3^+ is afforded by a comparison of R_{CN}=0.006±0.001 in OMC1 and R_{CN}=0.023±0.01 (Greason, Wootten and Loren 1985) in TMC1. The relatively weak drop in deuterium enhancement with increasing cloud temperature suggests that the deuterium reservoir responsible for enhancement has a higher value of dE than that of reaction (2). Reaction (3) can nicely account for the difference.

We conclude that deuteration of CH_3^+, most likely via reaction (3) operates in interstellar clouds and most likely constitutes a major source of deuterium fractionation in HCN in the warmer clouds. Now we explore the ramifications of this conclusion.

3. THE ELECTRON ABUNDANCE

A major destructive agent of most molecular ions is electron recombination. In the past, this was thought to dominate H_3^+ destruction, allowing limits to be set on the electron abundance from the H_2D^+/H_3^+ abundance ratio, which were estimated from DCO^+/HCO^+ abundance ratios. Michels and Hobbs (1984), however, calculated that cold vibrationally unexcited H_3^+ ions should have a very small recombination cross section. Smith and Adams (1984) corroborated this expectation, finding that they were unable to measure H_3^+ recombination at 95K. They noted that, owing to the low recombination rate, destruction of H_3^+ by other molecules such as CO, HD or N_2 dominated its demise, and therefore the DCO^+/HCO^+ ratio was removed as an effective indicator of electron abundance.

Unlike H_3^+, the recombination coefficient for CH_5^+, and presumably CH_3^+, does not vanish at low temperatures (Smith and Adams 1984). Electron recombination, therefore, remains an important process for the destruction of CH_2D^+ at low temperatures. A number of common neutrals (such as CO, N_2 and H_2O) have no reaction with CH_3^+. The most significant sinks for CH_3^+ are probably reaction with CI leading to C_2H^+ (and possibly eventually to CCD) and radiative association with H_2. To the extent to which the DCN/HCN ratio derives from the CH_2D^+/CH_3^+ ratio then, we might be able to measure limits to electron abundances from [DCN]/[HCN]. The figure shows the calculated [DCN]/[HCN] ratio, assuming contributions from both H_2D^+ and CH_2D^+.

At very cold temperatures, H_2D^+ dominates and the abundance of that molecule is controlled by its destruction by abundant neutrals. Here we use $X_i=9\times10^{-5}$, as one might expect, for example, for CO. At warmer temperatures, CH_2D^+ dominates DCN creation. Unfortunately, considering only the colder clouds the strict upper limits derived for X_e and X(CI) are not very interesting, $X_e<8\times10^{-7}$ and $X(CI)<1.4\times10^{-3}$ respectively. These limits ignore radiative association, which is probably the dominant destructive reaction for CH_2D^+. If we assume radiative association to be the dominant destroyer of CH_2D^+, we can estimate an upper limit to the rate of the $CH_2D^+ + H_2 \rightarrow CH_4D^+ + h\nu$ reaction to be 2.6×10^{-11} cm^3 s^{-1}. This is comfortably far above the measured rate of 1.8×10^{-13} cm^3 s^{-1} at 13K (Barlow, Dunn and Schaver 1984, and suggests that the role of CI and electrons may be unimportant. Other estimates of the electron abundance reinforce this view.

Smith and Adams (1984) estimated a value for the electron abundance in TMC1 from the data of Guelin et al. (1982) by assuming a value for the cosmic ray ionization rate in clouds, an abundance for HCO^+ (derived from measurements of the rare $HC^{18}O^+$ isotope), and a measure for the density. They estimated that $X_e \sim 4\times10^{-7}$ for TMC1.

Fortunately, the detection of H_2D^+ emission by Phillips et al. (1985) toward NGC2264 (it was not detected toward TMC1) measures the abundance of H_3^+ in that direction. This, in turn, strongly constrains the HCO^+ abundance, and the electron abundance can be calculated in a straightforward manner from measurement of the $X(H^{13}CO^+)/X(^{13}CO)$ ratio. Thus $Zn = X(H^{13}CO^+)/X(^{13}CO) = kX(H_3^+)/(\beta X_e + \delta)$, where $k = 1.8\times10^{-9}$ cm^3 s^{-1} (Adams and Smith 1981), $X(H_3^+) = (0.7-2.3)\times10^{-9}$ (Phillips et al. 1985), β is the electron recombination coefficient for HCO^+, and $\delta = \Sigma\, k_i X_i$ is the destruction rate for HCO^+ by neutral reactions with species X_i. Wootten, Snell and Evans (1980) measured $X(H^{13}CO^+)/X(^{13}CO) = 7.5\times10^{-5}$ in NGC2264 at a velocity of 8 km s^{-1}. At the 6.5 km s^{-1} velocity characteristic of the DCO^+ or H_2D^+ emission we estimate that the ratio is only slightly smaller. Then

$$X_e < \frac{kX(H_3^+)}{(Zn)\beta} = 5\times10^{-8}$$

where the limit results from ignoring δ. Thus, the H_2D^+ observation, which we believe to be the most reliable method for determination of Xe, results in values quite similar to those derived from $[DCO^+]/[HCO^+]$ using erroneous recombination coefficients! We conclude that the [DCN]/[HCN] observations require more efficient destruction of CH_2D^+ than is possible through electron recombination or ion-molecule reactions, and probably constitute good evidence that radiative association reactions are important in interstellar clouds.

4. DEUTERATED MOLECULES AS TRACERS OF THE [D]/[H] ABUNDANCE RATIO

We conclude that the observations suggest that CH_2D^+ is an important vehicle for molecule deuteration in warm clouds. In the nearby GMCs we have surveyed, the near constancy of [DCN]/[HCN] is consistent with a nearly constant ratio for $[CH_2D^+]/[CH_3^+]$. This latter ratio is relatively free of temperature effects, since most GMC temperatures lie below 45K. Furthermore, we have shown that the electron abundance in at least one cloud is too low for electron recombination to be an important sink for CH_2D^+. Observations suggest a level for the neutral carbon abundance which is also too low for electron recombination to dominate CH_2D^+ destruction. Radiative association, which is independent of the (poorly determined) abundances of trace species, probably dominates CH_2D^+ destruction. Therefore, the [DCN]/[HCN] ratio

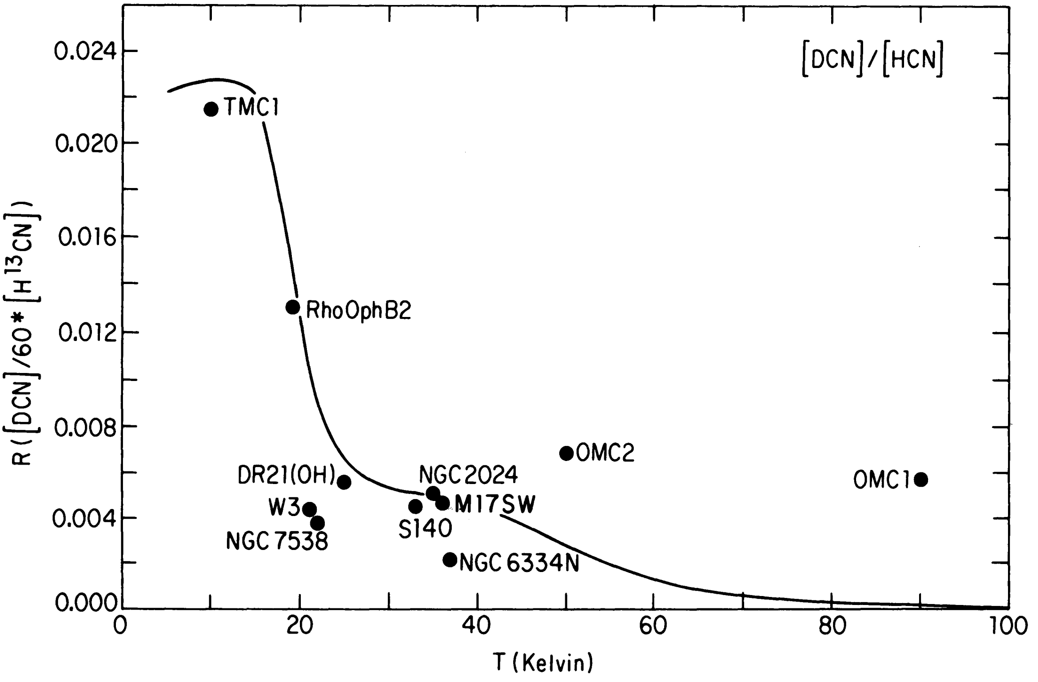

Figure 1. The temperature dependence of the [DCN]/[HCN] ratio, from data in Greason, Wootten and Loren (1985). The solid line superimposed shows the expected temperature dependence if deuteration in DCN derives from both H_2D^+, which dominates at lower temperatures, and from CH_3^+, which dominates at the warmer temperatures. Here we assume that destruction of CH_3^+ is dominated by radiative association, by recombination with electrons and by reactions with neutral carbon.

is relatively free of the effects of local cloud conditions, and is more likely than the abundance ratios of other deuterated species to reflect the local abundance of HD, and presumably [D]/[H]. The [DCN]/[HCN] ratio probably constitutes the best available probe of galactic [D]/[H] abundance gradients, and the [DCN]/[HCN] gradient observed by Penzias (1979) seems likely to reflect an underlying galactic gradient in [D]/[H]. We note that with current technology, an instrument such as the Millimeter Array under study at NRAO could measure [DCN]/[HCN] in GMCs in nearby galaxies.

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DISCUSSION

GLASSGOLD: If the H_2D^+ measurement in NGC 2264 turns out not to be a detection, which way will your estimate of X_e change in this cloud?
WOOTTEN: X_e depends linearly on $X(H_3^+)$, so if $X(H_3^+)$ proves to be lower, the upper limit of X_e will be lowered accordingly.

AVERY: Very recently we have detected the strongest hyperfine component of the ground state transition of C_2D in TMC-1. I don't have the corresponding abundance with me, but the C_2D/C_2H ratio is quite large if we take your earlier estimate of [C_2H] in TMC-1. But the estimate of [C_2H] in your TMC-1 paper of 3 or 4 years ago is probably too low because of optical depth effects.
WOOTTEN: I agree completely. All the deuterium enhancements in TMC-1 are consistent. I'll wager a lakh (10^5) of deuterium atoms that [CCD]/[CCH] $\cong$ 0.02.

FRIBERG: We have measured all the hyperfine components of the N = 1-0 C_2H transition in TMC-1. They are equally strong indicating an optical depth of atleast ten.
WOOTTEN: That confirms that estimate of deuterium enhancement cannot be made without measurements of ^{13}C - substituted species.