THE CHEMISTRY OF COLD, DARK INTERSTELLAR CLOUDS

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ABSTRACT. In recent years the nearby cold, dark clouds have been shown to possess a rich chemistry, with interesting differences with respect to warmer massive-star-forming regions and also among the cold clouds themselves. 39 molecular species are now known in these regions. Recent molecular detections and upper limits in dark clouds are discussed, with particular emphasis on the tri-carbon species C_3O, C_3H, and C_3H_2.

The dark clouds as described here are relatively nearby, moderately dense (10^3-10^5 H_2 molecules per cm^3), very cold ($T_k \simeq 10K$) clumps of interstellar matter. They may be either condensations within a large complex of material (e.g. in the Taurus region) or isolated clouds such as Bok globules (e.g., B335). Well studied clouds such as TMC-1 and L134N (= L183) have masses of order $100M_{\odot}$, but may have a complex substructure in which individual components have much smaller masses. Some appear to have associated low luminosity infrared sources, which may be protostars. The physical and chemical properties of such regions have been summarized by, among others, Winnewisser (1981), Irvine et al., (1985), Myers (1985), and Leung (1985). In the last few years it has become increasingly apparent that these dark dust clouds have a rich chemistry which rivals in complexity that of the better known, warmer, and more massive clouds such as Sgr B2 and Ori A. Some 39 of the presently known 69 interstellar molecules have been observed in dark clouds (Table I), and the ratio increases to 39/61 if we exclude molecular species found only in stellar envelopes or for which the identification is uncertain. These cold regions are particularly important for astrochemistry, because they provide straight-foward tests of theoretical models: their quiescent, low temperature nature implies that we may neglect processes such as shock heating, grain mantle evaporation, and interaction with stellar winds which are clearly present in more massive star-forming regions. Although the structure of dark clouds may be complicated, it is unquestionably much more homogeneous than that in sources such as Orion KL, and their investigation is further aided by the high spatial resolution made possible by the

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TABLE I: MOLECULES IDENTIFIED IN DARK CLOUDS[a]

SIMPLE HYDRIDES, OXIDES, SULFIDES, AMIDES, AND RELATED MOLECULES:

H_2 [b]	SO	CS	NH_3
OH	SO_2	CC	
CH	OCS	CO	

NITRILES, ACETYLENE DERIVATIVES, AND RELATED MOLECULES:

CN	HCN	H_3C-CN	$H_2C=CH-CN$
$C\equiv CH$	$HC\equiv C-CN$	$H_3C-C\equiv C-CN$	HN=C
$C\equiv C-C\equiv CH$	$H(C\equiv C)_2-CN$	$H_3C-C\equiv CH$	HN=C=O
$C\equiv C-CN$	$H(C\equiv C)_3-CN$	$H_3C-(C\equiv C)_2-H$	
$C\equiv C-CO$	$H(C\equiv C)_4-CN$	$H_3C-(C\equiv C)_2-CN$?	
$C\equiv C-CH$	$H(C\equiv C)_5-CN$		

ALDEHYDES, ALCOHOLS, ETHERS, KETONES, AND RELATED MOLECULES:

$H_2C=O$	$H_2C=C=O$?
$H_2C=S$	H_3COH
$H_3C-CH=O$	

CYCLIC MOLECULES:	IONS:	
C_3H_2	$HC=O^+$	HN_2^+
	$HC=S^+$	

[a] Irvine *et al.* (1985), Hjalmarson (1985) and new results in text.
[b] Not observed directly, but surely the dominant constituent.

TABLE II: UPPER LIMITS ON ABUNDANCES IN TMC-1

Molecule	Transition Observed	Total Column Density (cm^{-2})	Fractional Abundance
SiO	1-0	$<5(10)^{10}$	$<5(10)^{-12}$
CCO	5(4)-4(3) [a] [c]	$1-3(10)^{12}$	$1-3(10)^{-10}$
HCCN	5(4)-4(3) [a]	$1(10)^{12}$	10^{-10}
CH_3CH_2CCH	4(1,4)-3(1,3)	$3(10)^{13}$	$3(10)^{-9}$
CH_2CHC_3N	9(0,9)-8(0,8)	$3(10)^{12}$	$3(10)^{-10}$
CH_3NC	1(0)-0(0)	$5(10)^{11}$ [b]	$5(10)^{-11}$ [b]
H_2CCNH	1(0,1)-0(0,0)	$5(10)^{12}$	$5(10)^{-10}$
$HCCNH_2$	1(0,1)-0(0,0)		

RA(1950) = $04^h38^m38.6^s$, DEC = 25°35'45"; assumes T_{exc} = 5-10K and $N(H_2) = 10^{22}$ cm^{-2}; cf. Irvine *et al.* (1985). References: SiO and CCO (Friberg, Ziurys, and Irvine, unpublished FCRAO data); HCCN (Suzuki *et al.*, 1985); CH_3CH_2CCH (Hjalmarson and Irvine, unpublished Onsala data); CH_2CHC_3N (Kroto *et al.*, 1985); CH_3NC (Irvine and Schloerb, 1984); H_2CCNH and $HCCNH_2$ (R.D. Brown, *et al.*, unpublished NRAO 43m and FCRAO (5(0,5)-4(0,4)) data; $HCCNH_2$ data currently being reduced). See also Saebø *et al.* (1984, $HCCNH_2$); Yamada *et al.* (1985, CCO); Rodler *et al.* (1984, H_2CCNH).
[a] J(N); [b] Marginal Detection; [c] 2(1)-1(0) upper limit obtained at Haystack Observatory (Madden and Irvine, unpublished).

relatively small distance from the sun for the well studied dark clouds. Moreover, the small velocity gradients in these regions result in line widths which are in some cases only slightly greater than the thermal width, providing "laboratories" in which basic molecular parameters may be determined with an accuracy often considerably higher than is possible in the terrestrial laboratory, particularly for the growing number of highly reactive radicals and ions identified (e.g., C_3H; Thaddeus et al., 1985a).

Studies of dark cloud composition have included searches for heavy species previously known only in the giant molecular clouds. In three recent examples, approximately equal abundances were found in the two clouds TMC-1 and L134N, which exhibit striking contrasts for other chemical species (e.g., Irvine et al., 1985). Detection of acetaldehyde (CH_3CHO) in these sources has recently been published (Matthews et al., 1985), while the rather strong emission from methanol (CH_3OH) is being described at this meeting by Friberg, and the identification of carbonyl sulfide (OCS) is shown in Figure 1. The results make it clear that the inventory of heavy molecules in TMC-1 is not restricted to nitriles and highly unsaturated molecules.

The dark clouds are also becoming an important hunting ground for new interstellar molecules. These include not only the heaviest cyanopolyynes (cf. the recent detection of $HC_{11}N$ by Matthews and Bell, 1985) and methylated relatives such as CH_3C_4H (reported by several authors), but also the interesting group of tricarbon compounds C_3O, C_3H, and C_3H_2. These latter three are all "non-terrestrial", in the sense that they were either discovered in space before being observed in the laboratory (C_3H and C_3H_2) or their laboratory detection occurred only immediately prior to astronomical observations (C_3O). Tricarbon monoxide (C_3O) presents an important example of the intimate interaction between theoretical quantum chemistry, laboratory experiments, and astronomical observations: accurate ab initio calculations made possible detection of the rotational spectrum of C_3O in the laboratory; and only the additional accuracy of the laboratory data allowed for the observation of the weak astronomical emission lines (Brown et al., 1985). The radical C_3H (propynylidyne) is one of a number of molecular fragments initially identified in the spectrum of the evolved carbon star IRC+10216 and subsequently found to be present also in the cold cloud TMC-1 (Thaddeus et al., 1985a). To date, C_3H is known only in these two sources, while tricarbon monoxide has been found only in TMC-1 itself. These two molecules present the interesting contrast that their abundance in TMC-1 appears in one case (C_3O) to agree very well with standard gas phase ion-molecule calculations (Brown et al., 1985; Herbst et al., 1984), while in the other (C_3H) it seems to be substantially below similar predictions (Millar and Freeman, 1984).

In contrast, cyclopropenylidene (C_3H_2) appears to be virtually ubiquitous in the Galactic interstellar medium (Matthews and Irvine, 1985). Any lingering doubt about the assignment of lines to this species in TMC-1 can be laid to rest with the detection illustrated here for the 2_{20}-2_{11} transition, at precisely the frequency predicted on the basis of laboratory and previous astronomical observa-

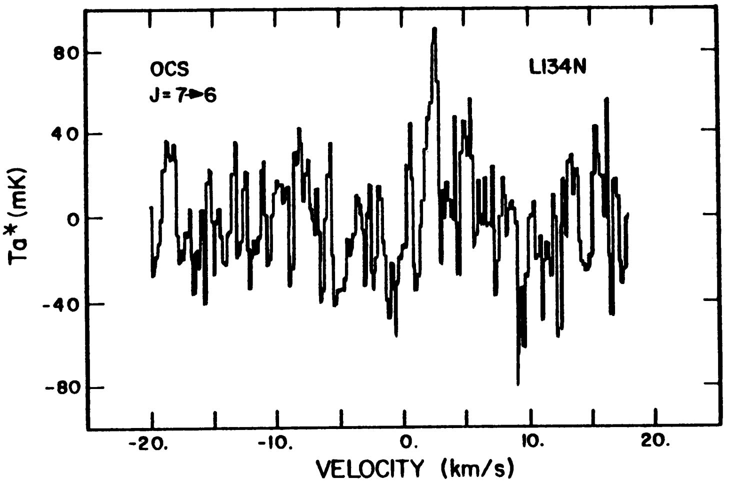

Figure 1. Detection of OCS in the dark cloud L134N (RA = $15^h51^m24^s$, DEC = -02°44'19", 1950). Similar antenna temperature observed at TMC-1 cyanopolyyne peak. Unpublished FCRAO data (see MacLeod et al., 1985).

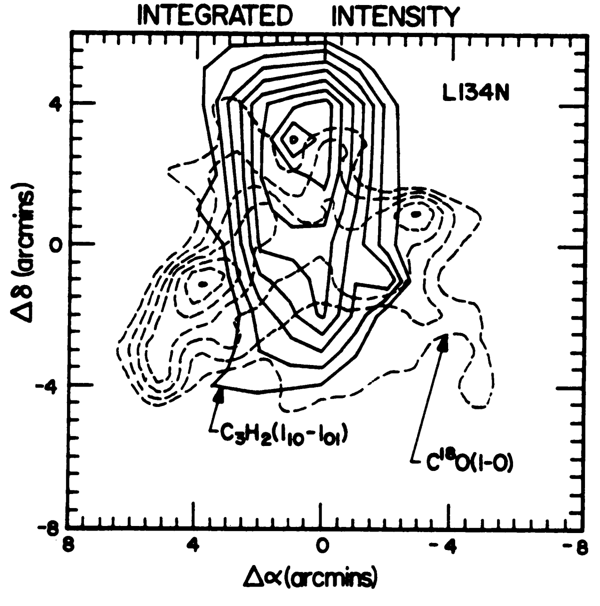

Figure 3. Maps of C_3H_2 (1_{10}-1_{01}) and $C^{18}O$ (1-0) emission in L134N obtained at NRAO 43m and FCRAO 14m telescopes, respectively. Reference position is RA(1950) = $15^h51^m30^s$, DEC = -02°43'31". Cf. Swade, (1986).

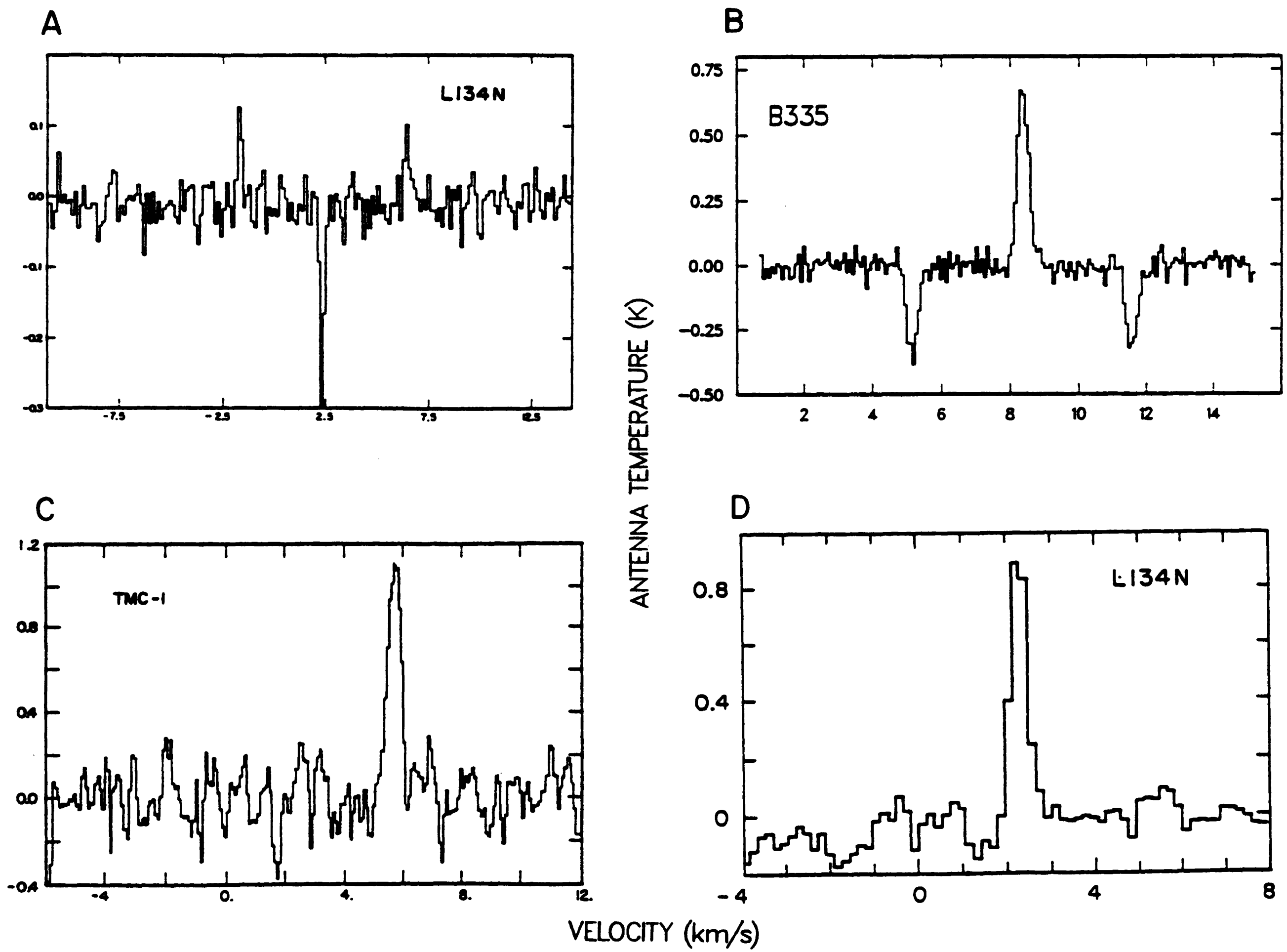

Figure 2. Several transitions of C_3H_2 in various dark clouds. A) $2_{20}-2_{11}$; B) $1_{10}-1_{01}$; C) $2_{11}-2_{02}$; D) $2_{12}-1_{01}$. Cf. Matthews and Irvine (1985) and unpublished data from FCRAO and NRAO.

tions (Figure 2; Thaddeus et al., 1985b). In addition to its chemical interest as the first interstellar hydrocarbon ring, C_3H_2 promises to provide a very important probe of physical conditions in dark clouds. As has been predicted by Avery (this meeting), the 2_{20}-2_{11} transition is seen in absorption for the density conditions applicable to typical dark clouds, in contrast to other transitions which are seen in emission (Figure 2). In many cases when a continuum source is present, the 1_{10}-1_{01} transition at 18 GHz exhibits both emission toward the molecular cloud-HII region, and absorption apparently due to intervening lower excitation material (Matthews and Irvine, 1985). Whether such absorbing regions are similar to the dark clouds discussed here but at greater distances, or are lower density "HI clouds", is uncertain (Nyman, 1983; Batrla et al., 1984).

Molecular species which have not been detected in dark clouds also provide important constraints on chemical models. Some recent examples for which sensitive data are available are listed in Table II. Note, for example, that SiO is more than two orders of magnitude less abundant than in the warm gas toward Orion KL, quite probably reflecting depletion of silicon into the interstellar grains. Likewise, the failure to detect the dicarbon species C_2O and HC_2N is in accord with a model for building interstellar carbon chains in which the length of such chains grows by the addition of acetylenic units. It is also of interest that, although both C_4H and CH_3C_4H are known in TMC-1, the more saturated ethyl acetylene (CH_3CH_2CCH) has not been found in dark clouds. Likewise, the similar abundances of the chemical isomers HCN and HNC has provoked considerable theoretical and laboratory analysis (e.g., Irvine et al., 1985), but attempts to detect any of three stable isomers of methylcyanide (CH_3CN) have not been successful (cf. DeFrees et al., 1985).

Detailed comparison of observation and theory requires us to not simply inventory the molecular species present in dark clouds, but to determine accurate relative abundances. Values for TMC-1 and L134N have been tabulated by Irvine et al. (1985) and updated by Hjalmarson (1985), who discuss the differences between dark cloud chemistry and that in warmer, less quiescent regions. There are also interesting chemical contrasts among the dark clouds themselves, as well as poorly understood variations within a given cold cloud. Figure 3 shows the intensity distribution within the core of L134N for $C_{18}O$, which should trace the total column density of molecular gas, and C_3H_2 (1_{10}-1_{01}), which shows a completely different distribution. The latter is quite similar to that found for NH_3 (1,1). Although this might be thought to reflect simply a difference in excitation conditions (primarily molecular hydrogen density), similar maps for other species provide strong evidence that there are actual chemical gradients within this cloud core (Swade, 1986).

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DISCUSSION

TURNER: The lowest para transition of C_3H_2 at 82.9 GHz is conspicuously absent in SgrB2, the only source for which many (7) lines attributed to C_3H_2 (out of 10 expected) have been seen. Thus it is of interest that you have detected the next-highest para transition at 21 GHz in the dark cloud TMC-1, whose excitation is much lower than that of SgrB2. Has the 82.9 GHz line been searched in TMC-1? Its presence or absence might not bear necessarily on the identification of these lines as C_3H_2 is clearly anomalously excited in many sources, perhaps the excitation of the lowest para transition might also be unusual.
IRVINE: The 82 GHz line has not, to my knowledge, been sought in dark clouds. I believe, however that the lowest energy para - C_3H_2 transition (to the 0_{OO} level) occurs at 51 GHz and is thus blocked by atmospheric oxygen. The 18 GHz line appears to be thermalized in dark clouds.

LEGER: What is the estimated abundance of C_3H_2?
IRVINE: In TMC-1, for which several transitions have been observed, a lower limit on the abundance is probably $\sim 10^{-8}$, although the data is very new and further analysis is needed.

GLASSGOLD: Would you comment on the underlying chemical problems caused by the detailed observations of the TMC-1 cloud from the observers point of view?
IRVINE: The prevalence of chemically unsaturated carbon chains in regions like TMC-1 is surely significant, and may relate to the difficulty of producing hydrogenation in the gas phase (cf, paper by Herbst). The abundance of as yet undetected, heavy asymmetric states (H-C-O species) should also provide important clues to chemical processes. Finally, there are still strong unidentified lines in dark clouds, suggesting the presence of other "non-terrestrial" species.