

INTERSTELLAR ICES AS A SOURCE OF CN-BEARING MOLECULES IN PROTOPLANETARY DISKS

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Abstract. A reliable model for the composition and evolution of interstellar ices in regions of active star formation is fundamental to our quest to determine the organic inventory of planetesimals in the early Solar System. This has become a realistic goal since the launch of the Infrared Space Observatory, which provides a facility for infrared spectroscopy unhindered by telluric absorption over the entire spectral range of vibrational modes in solids of exobiological interest. Interstellar molecules detected in the solid phase to date include H₂O, NH₃, CO, CO₂, CH₃OH, CH₄, H₂CO, OCS and HCOOH, together with a C≡N-bonded absorber generically termed 'XCN'. In this article, we focus on cosmic synthesis of CN-bearing species, as this important class of prebiotic molecules may not have formed endogenously in significant quantities on early Earth if conditions were not highly reducing. Experiments in which interstellar ice analogs are subject to UV photolysis or energetic ion bombardment yield CN-rich residues with a spectral signature that matches a corresponding feature observed in young protostars enshrouded in dust and gas. CN-bearing species are also present in cometary ices, with a combined abundance comparable to the lower end of the range observed in protostars. Energetic processing of interstellar ices is thus a viable and potentially significant source of CN compounds in protoplanetary disks.

Keywords: cyanogen, interstellar molecules, protoplanetary disks, protostars

1. Introduction

The availability of CN-bearing molecules on the early Earth is an important issue in the origins of life. Of all key prebiotic molecules, those containing the cyanogen (C≡N) bond are the hardest to produce in situ in an environment that is not overly reducing. Hydrogen cyanide (HCN), a key intermediary in the production of amino acids, is readily formed by Miller-Urey-type synthesis in a reducing atmosphere containing CH₄ and NH₃ (e.g. Miller, 1992 and references therein). However, the production rate of HCN is reduced dramatically in an atmosphere in which the primary carbon source is CO₂ and the primary nitrogen source is N₂ (Kasting, 1993), due to the higher binding energies of these molecules. Geochemical evidence provides support for a non-reducing archaean atmosphere, at least to 3.8 Gyr before present (Schopf, 1992; Kasting *et al.*, 1993; Delano, 1993, 2001). This finding motivates a search for extraterrestrial sources of CN-bearing



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prebiotic molecules. Possible production sites include primitive Solar-System bodies (Matthews, 2000) and interstellar clouds.

2. Interstellar 'XCN'

Several $C\equiv N$ bonded species are known to exist in the gaseous component of the interstellar medium, via detection of rotational spectral lines at radio wavelengths identified with molecules such as HCN, CH_3CN (methyl cyanide), CH_2CHCN (vinyl cyanide) and CH_3CH_2CN (ethyl cyanide) (Snyder, 1997). Their abundances are generally low ($<10^{-8}$ with respect to hydrogen) in cold molecular clouds, but tend to be enhanced by factors of 10 or more in 'hot core' regions surrounding protostars where evaporation from grains may contribute to gas phase abundances (e.g. Blake *et al.*, 1987; van Dishoeck and Blake, 1998). Gaseous CH_2CHCN and CH_3CH_2CN have been shown to concentrate within a region small compared with the Oort cloud (the domain of comets in our Solar System) in the envelope of a protostar in the Sgr B2 molecular cloud (Liu and Snyder, 1999). These results support the view that grain evaporation may be a major source of CN-bonded gas-phase molecules in protoplanetary disks.

CN-bearing molecules do, indeed, appear to be present in the solid phase of interstellar matter, as a component of the ice mantles on dust grains in dense molecular clouds. They are detected by means of an infrared spectral absorption feature centered at $4.62\ \mu\text{m}$ (Lacy *et al.*, 1984; Tegler *et al.*, 1995; Pendleton *et al.*, 1999). This 'XCN' feature* (Figure 1) is detected only toward dust-embedded protostars and not in lines of sight that sample cold, quiescent molecular clouds or diffuse regions of the interstellar medium (Whittet *et al.*, 2000). This finding strongly suggests that the absorber is a product of reactions that occur in the environments of the newly-formed stars themselves. Energetic processing (UV irradiation or energetic ion bombardment) of interstellar ices may lead to synthesis of complex organic molecules, including CN-bonded species (Tielens and Charnley, 1997). Laboratory analog experiments have shown that ices that initially contain species such as H_2O , CO , CH_4 , and CH_3OH , together with NH_3 as the nitrogen source, produce residues capable of reproducing the observed feature after exposure to UV photons or high-energy protons (Lacy *et al.*, 1984; Bernstein *et al.*, 1995; Elsila *et al.*, 1997; Pendleton *et al.*, 1999; Palumbo *et al.*, 2000). Thus, it appears that CN-bearing species may be a natural product of the evolution of material surrounding a newly-formed star. Recent confirmation of the presence of NH_3 in interstellar ices (Lacy *et al.*, 1998; Gibb *et al.*, 2000; Chiar *et al.*, 2000) adds weight to this conclusion.

* The absorber that produces the $4.62\ \mu\text{m}$ ($2165\ \text{cm}^{-1}$) feature is not uniquely identified; it is referred to generically as 'XCN' in the astronomical literature, where X is unknown and $-C\equiv N$ bonding is implied.

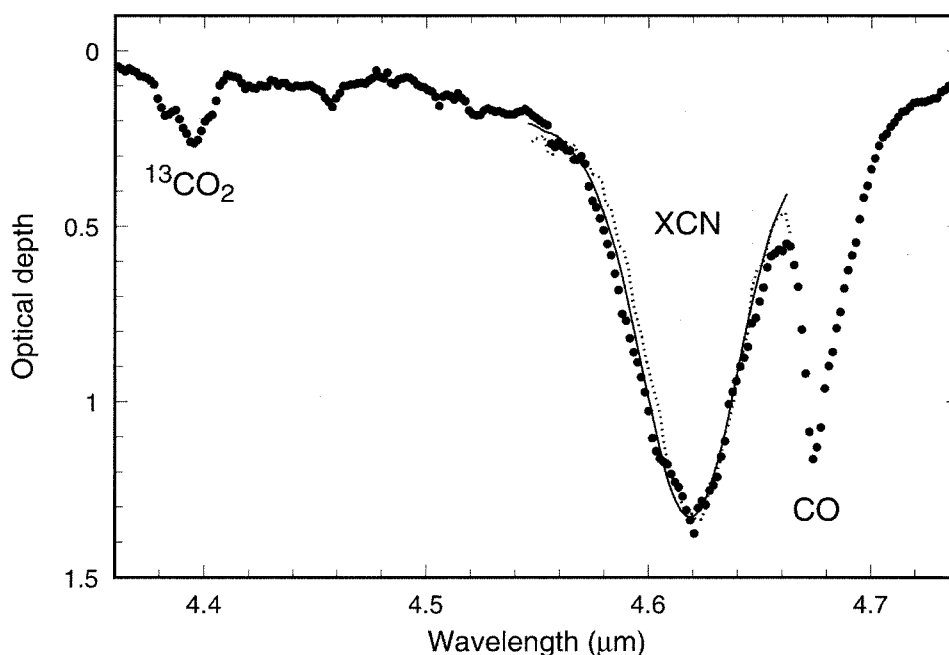


Figure 1. Infrared spectrum of the protostar W33A (points) in the region of the $C\equiv N$ vibrational stretching feature, obtained with the short wavelength spectrometer of the Infrared Space Observatory (Gibb *et al.*, 2000). Also shown for comparison are laboratory spectra of interstellar ice analogs after exposure to UV radiation (dotted curve; Bernstein *et al.*, 1995) and proton bombardment (solid curve; Palumbo *et al.*, 2000).

The astronomical observations (Figure 1) allow constraints to be placed on the abundances of various CN-bearing species that might be candidates for ‘XCN’. These include both cyanides (nitriles, isonitriles) and cyanates. Laboratory spectra covering the $C\equiv N$ stretch region for several nitriles ($X-C\equiv N$) frozen in an H_2O -ice matrix are presented by Bernstein *et al.* (1997, their figure 4). Absorption features are typically 20 cm^{-1} ($0.04\text{ }\mu\text{m}$) in width, with peak position ranging from 4.42 to $4.57\text{ }\mu\text{m}$ (the majority lying between 4.42 and $4.50\text{ }\mu\text{m}$). If a variety of nitriles are present in interstellar ices, a broad, composite feature centered at $\sim 4.47\text{ }\mu\text{m}$ is predicted. However, the observed spectrum clearly shows that the principal interstellar absorption is centered near $4.62\text{ }\mu\text{m}$ and extends roughly from 4.55 to $4.7\text{ }\mu\text{m}$. Weak structure may exist in the 4.50 – $4.57\text{ }\mu\text{m}$ region, on the shoulder of the deep feature, that might be attributed to nitrile absorption. However, no features are seen in the 4.42 – $4.50\text{ }\mu\text{m}$ region, where the majority of nitriles have their CN signatures. Isonitriles ($X-N\equiv C$) appear to be better candidates for the interstellar feature than nitriles in terms of spectral properties (Bernstein *et al.*, 1997; Pendleton *et al.*, 1999), as their absorptions lie closer to the observed $4.62\text{ }\mu\text{m}$ feature. However, the strength of the observed feature, together with the weakness of any absorption at shorter wavelength (Figure 1), implies a nitrile/isonitrile abundance ratio < 0.1 .

(Gibb *et al.*, 2000). Such a low abundance of nitriles relative to isonitriles seems highly implausible, given the greater stability of the former, and this argues against assignment of the XCN feature to isonitriles.

Species with cyanate ($-\text{O}-\text{C}\equiv\text{N}$) bonding appear to be the candidates most consistent with existing spectroscopic constraints (Pendleton *et al.*, 1999). These include the OCN^- ion (Grim and Greenberg, 1987; Schutte and Greenberg, 1997; Demyk *et al.*, 1998) and $-\text{O}-\text{C}\equiv\text{N}$ groups attached to organic residues (Palumbo *et al.*, 2000). A laboratory spectrum of such a residue is compared with the astronomical data in Figure 1 (solid curve). If this identification is correct, we should expect to detect cyanates in the gas phase in hot cores with abundances exceeding those of cyanides.

3. From Interstellar to Cometary Ices

Table I compares abundances for XCN and other molecules detected in the spectra of several well-studied infrared sources. These include Elias 16 (a red-giant field star situated behind a dark cloud), and four dust-embedded protostars (NGC 7538 IRS9, GL 7009S, W33A and GL 2136). XCN abundances are determined assuming a band strength for the cyanate (OCN^-) ion (Schutte and Greenberg, 1997). Abundances inferred for ices in comet C/1995 O1 (Hale-Bopp) are also given for comparison. All results are expressed as a percentage of the H_2O column density toward each source. The infrared sources are ordered from left to right in a probable sequence of increasing thermal processing of the ices, as indicated by the abundance of CO, the most volatile species represented. Elias 16 is believed to sample cold, quiescent material undisturbed by local star-formation activity (e.g. Whittet *et al.*, 1998 and references therein), whereas ices in the vicinity of protostars may be subject to heating and/or radiative processing (e.g. van Dishoeck and Blake, 1998). In interpreting Table I, it should be noted that thermal and energetic (radiative) processing are not necessarily coeval in an interstellar cloud. Ices may be heated by infrared radiation whilst remaining shielded from more energetic photons; conversely, in different circumstances, they may be subject to ultraviolet irradiation yet experience little heating.

It is interesting to compare the relative abundances of CH-, CO- and CN-bonded carbon in interstellar ices. In its entirety, of course, the interstellar medium is an overwhelmingly reducing environment, hydrogen outnumbering the next most abundant reactive elements (C, N, O) by factors of 10^3 – 10^5 . However, much of the hydrogen in interstellar clouds is in the form of gaseous H_2 , which will generally neither freeze out nor readily participate in chemical reactions on grain surfaces. The most abundant gas phase molecule to become attached to grain surfaces is CO, and this is typically more abundant than gas phase CH by factors of 10–100 due to its greater stability (larger binding energy). Results in Table I indicate that, together, CO and CO_2 (the oxidation product of CO) account for a substantial fraction of

TABLE I

Abundances (expressed as percentages relative to H₂O) for XCN and other molecules present in the ices toward interstellar infrared sources and comet Hale-Bopp. Interstellar and cometary data are from the compilations of Gibb *et al.* (2000) and Bockelée-Morvan *et al.* (2000), respectively. Elias 16 is a background star situated behind a cold molecular cloud. NGC 7538 IRS9, GL 7009S, W33A and GL 2136 are dust-embedded protostars. The interstellar sources are displayed in sequence of decreasing CO abundance (which implies a sequence of increasing ice temperature). Results for XCN in astrophysical spectra depend on an assumed band strength based on laboratory data for the cyanate ion. In the case of Hale-Bopp, the XCN abundance represents the sum of detected CN-bearing species: HCN (0.25%), HNC (0.04%), HNCO (0.1%), CH₃CN (0.02%) and HC₃N (0.02%)

Species	Elias 16	NGC 7538 IRS9	GL 7009S	W33A	GL 2136	Comet Hale-Bopp
H ₂ O	100	100	100	100	100	100
CO	25	16	15	8	2	23
CO ₂	18	22	21	13	16	6
CH ₄	–	2	4	1.5	–	0.6
CH ₃ OH	<3	5	30	18	6	2.4
H ₂ CO	–	4	3	6	3	1.1
HCOOH	–	3	–	7	–	0.1
OCS	<0.2	–	0.2	0.2	–	0.4
NH ₃	<9	13	–	15	–	0.7
XCN	<0.5	1	1.5	3.5	0.3	0.4

the inventory of detected molecules in interstellar ices (e.g. ~40% in Elias 16, NGC 7538 IRS9 and GL 7009S). The CO₂ abundance remains rather constant over a range of interstellar environments, suggesting that the primary route(s) to its formation are robust and not strongly dependent on physical conditions (Whittet *et al.*, 1998). The CH₃OH abundance is, in contrast, highly variable. In the majority of objects studied to date, CH₃OH is less abundant than CO₂ (Gerakines *et al.*, 1999), but this situation is reversed toward the high-mass protostars GL 7009S and W33A (Dartois *et al.*, 1999).

The two sources with the highest CH₃OH abundances in Table I also have the highest XCN abundances. If XCN is, indeed, the product of energetic processing (photolysis and/or ion bombardment), the fact that the CH₃OH abundance behaves in a similar way suggests that it is likewise formed in regions where processing of the ices is important. Detailed studies of the spectral features of CO₂ in laboratory analogs show that annealing leads to the formation of CO₂-CH₃OH complexes in the ices that have spectral signatures matching those observed in protostars (Ehrenfreund *et al.*, 1998, 1999; Gerakines *et al.*, 1999; Boogert *et al.*, 2000). Heating therefore appears to be implicated in the production of CH₃OH-rich ices. CH₄, on

the other hand, has similar abundance in NGC 7538 IRS9, GL 7009S and W33A, suggesting that thermal or energetic processing is not an important factor in its formation: CH₄ presumably forms by hydrogenation of carbon not tied up in CO or CO₂.

Comets are the most primitive bodies in the Solar System, and potentially a major contributor to the volatile reservoirs of the terrestrial planets (e.g. Mumma, 1997; Whittet, 1997; Irvine *et al.*, 2000). They may be composed as least in part of dust/ice aggregates from the parental molecular cloud (e.g. Greenberg and Hage, 1990; Briggs *et al.*, 1992). The prevalence of presolar ices in a particular comet can be surmised from its composition. In the case of Hale-Bopp, high CO abundance compared with average cometary values is taken to suggest it to be a relatively pristine, unaltered comet, perhaps representative of the inventory of interstellar ices in the early Solar System.

Comparing interstellar and cometary abundances in Table I, some general similarities are evident, notably the dominance of CO and CO₂ over hydrogenated forms of carbon*. The CH₃OH abundance in Hale-Bopp is consistent with the upper limit determined for quiescent clouds and much lower than that toward massive protostars W33A and GL 7009S. Real comet-to-comet variations in CH₃OH abundance have been claimed, and these might reflect different levels of processing of interstellar ices in the solar nebula, prior to their incorporation into cometary nuclei (Mumma, 1997). In any case, it is reasonable to conclude that interstellar ices subsumed by the solar nebula were less thermally processed than those in the vicinity of massive protostars. The aggregate XCN abundance (~0.4%) seen in Hale-Bopp is consistent with this picture: it is comparable with the *lowest* values observed in protostars.

A surprising feature of Hale-Bopp (and of comets generally: Cottin *et al.*, 1999) is the dearth of NH₃. Indeed, the sum of all known N-bearing species falls well short of expectations based on the elemental abundance of nitrogen. The interstellar NH₃ abundance is not yet measured toward a sufficiently large sample of objects to determine whether the values listed in Table I are truly representative. It may be that N₂ is an important or even dominant form in both interstellar and cometary ices, but this is difficult to verify spectroscopically. Although most laboratory simulations of XCN production assume NH₃ as the nitrogen-donor, processing of ices in which NH₃ is replaced by N₂ also lead to XCN if ions are used as the energy source (Palumbo *et al.*, 2000). Exposure of presolar ices to the solar wind may thus have provided a mechanism for generating C≡N-bonded molecules in the early Solar System.

* The true CO/CO₂ abundance ratio in cometary ices is difficult to determine from observed emission rates, as one species gives rise to the other. The apparently low CO₂ abundance in Hale-Bopp relative to interstellar ices might be due to assumptions regarding the CO/CO₂ ratio as a function heliocentric distance (see Bockelée-Morvan *et al.*, 2000).

4. Future Prospects

It is clear from the astrophysical evidence that energetic processing of interstellar ices generates CN-bearing molecules in the circumstellar environments of massive protostars such as W33A. However, such massive objects will develop into hot, blue main-sequence stars with relatively short lifetimes (< 100 Myr), and they are not therefore considered favorable sites for the development of planetary life (Kasting, 1997). It will be important in the future to determine abundances for XCN and other organic molecules in the ices associated with lower-mass protostars that provide better analogs of the early Solar System. This is difficult because low-mass stars are intrinsically less luminous, and therefore require larger telescopes and more sensitive detectors to yield spectra of sufficient quality. Another approach is to study in detail the spatial distribution of gaseous molecules believed to have evaporated from the grains. The advent of millimeter-wavelength interferometric arrays should provide major advances in this field over the next 10–20 yr.

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