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Comparison of Interstellar and Cometary Molecular Abundances

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Relative molecular abundances of CN and C₂ determined for cometary atmospheres are compared with abundances computed for interstellar conditions, using rates obtained by other authors for gas-phase reactions in H I regions as well as for models with high density and temperature up to 5000 K. It is shown that observed relative abundances indicate some CN decrement in comets versus hypothetical prestellar nebula equilibrium abundances governed by gas-phase reactions only. If the cometary nucleus preserves the original relative concentration of free radicals then the role of dust grains in the molecular formation involving the processes in the prestellar nebula must be considered as dominant.

1. Introduction

The similarity of the composition of the cometary gaseous atmosphere to that of the interstellar molecules has recently been discussed, particularly by Shimizu [1]. Similarly, a relation between the chemical composition of the cometary and interstellar dust can be expected [2], [3]. Cometary nuclei and interstellar dust may be considered as particles where the physical binding between solid grains, icy grains and free radicals determines their structure and behaviour in the radiation field.

A preliminary survey of the present available results indicates that the cometary abundance of atomic H and diatomic molecules resembles that of interstellar constituents. Therefore, a direct comparison of the interstellar and cometary molecular abundances may shed the light on processes in the protostar matter because of a probability that comets are in some sense relicts of the primordial planetary nebula.

However, the presence in comets of relatively complex molecules as H₂O, NH₃, HNCO, HC₃N, which are observed in interstellar space, has only partly been proved. A large amount of H₂O can be assumed from recent H I and OH observations in the ultraviolet region. Transitions in the microwave region for some of 30 molecules, which can be expected to exist in cometary nuclei, were computed by Huebner [4]. Unfortunately, all attempts to detect these compounds by radioastronomical methods have failed, presumably because of beam dilution.

Serious discrepancies have been found also between the photodissociation

probability of assumed parent molecules of cometary radicals and scale lengths for parent particles in real cometary atmospheres [5], [6], and icy grains are proposed as a source of free radicals [7] more likely than polyatomic molecules. Therefore the existence of complex molecules in comets and their abundance relative to that of diatomic free radicals became one of the most interesting problems of the study of processes which took place in the early history of the Solar System.

2. Molecular Abundances in Cometary Atmospheres

A direct, sufficiently accurate comparison between various diatomic molecules observed in interstellar matter and in comets can be made for CN, C₂ and, to some extent, for CO. The data for these and other molecules for several comets have been discussed by Arpigny [8] and partly by Vanýsek [9]. Only data for CN and C₂ obtained by photoelectric method (except for Comet Humason 1961e) summarized in Table 1 have been used in the following discussion.

Table 1. Relative Molecular Abundances in Comets

Comet	\bar{r} (AU)	ρ (km)*)	$F[(C_2)/(CN)]$	C ₂ /CN	Sequence**)	Reference
1964h	0.8	6×10^4	0.67	9.0	$\Delta v = +1$	[24]
1965f	1.0	1.2×10^5	1.06	11.8	$\Delta v = +1$	[25]
1966e†)	1.1	10^5	0.7 to 1.0	6.8	$\Delta v = 0$	[26]
1967n	1.8	1.4×10^5	0.33	3.2	$\Delta v = +1$	[9]
1959k	1.0	—	—	0.8	—	[8]
1961e††)	2.6	—	[CO ⁺]/[CN] $\sim 10^3$			[8]

In this small set of data the relative abundance [CN]/[C₂] varies in the range of 0.1 to 1.0.

The total number N of molecules of a given compound is determined by the luminosity $L_{\nu\nu'}$ of a particular band from the measured flux $F_{\nu\nu'}$ of the object at a geocentric distance Δ , i.e. $L_{\nu\nu'} = 4\pi\Delta^2 F_{\nu\nu'}$ and $N = L_{\nu\nu'} \alpha_{\nu\nu'}$. The emission coefficient is

$$\alpha_{\nu\nu'} = \frac{\pi e^2}{m_e h \nu} f p \rho(\nu, r)$$

where beside common symbols for the electron charge, mass and frequency, the other values are the oscillator strength f , the vibrational transition probability p and the radiation density of the solar field $\rho(\nu, r)$ for a given heliocentric distance.

*) ρ (km) is the linear distance corresponding to the size of the studied coma.

***) $\Delta v = +1$ or 0 gives the sequence of C₂ emission which was used to determine N(C₂).

†) $pf = 3.2 \times 10^{-2}$ for CN(0,0) and 2.7×10^{-3} for C₂(0,0).

††) [C₂]/[CN] unknown, but may be < 1 .

This simplified method introduced by Wurm [10] suits well CN abundances determined from the violet system. Molecules of C_2 , however, cannot be regarded as two-level systems and this approximative method is not quite exact.

Even if the resonance-fluorescence calculation shows that only by accidental numerical coincidence the use of fp as the oscillator strength for 1,0 transitions for the $\Delta v = +1$ sequence introduces no serious error, this would not be the case for another band. The simplified formula leads to overestimation of the C_2 abundance and according to Arpigny [8] should be corrected by the factor 0.4.

Experimental values for the oscillator strength for Swan bands can be grouped into two sets: the low values about 3×10^3 and the high ones about 8×10^{-3} . If a high f for $\Delta v = +1$ is used, then $[C_2]/[CN]$ will decrease about the factor 2 or somewhat more.

Although there are observational and theoretical uncertainties, it is evident that a low relative abundance of CN in comets is beyond any doubt.

Because the vibrational transition probability for Swan bands is $A_{vb} = 10^{-3}$ sec the relative intensities of C_2 emissions are essentially independent of heliocentric distances in considerable ranges and, therefore, $[CN]/[C_2]$ are not functions of r . Also the lifetimes of both molecules in the solar radiation field differ insignificantly and the scale lengths of C_2 and CN comas are comparable. The photodecomposition of CN cannot be considered as one possible effect which leads to the decreasing of the CN abundance.

The variation of $[CN]/[CO^+]$ or $[C_2]/[CO^+]$ should be considerably large. The abundance of CO^+ for a faint comet may be very often underestimated due to the dilution of the surface brightness of the ionic tail and a small f value. But the existence of faint comets "rich" in CO^+ , and some opposite cases as relatively bright comets, with an almost complete absence of the ionic tail, indicates a large variation of CO^+ and probably also of CO.

As a very typical example the results obtained by Arpigny [8] for Comet Bester (1947k) should be mentioned. Having corrected previous results obtained by Grudzinska [11] in regard to an appropriate interpretation of the f value, he found the ratio $[CO^+]/[CN] = 3$, while for the CO^+ "rich" comet Humason the same ratio is close to 10^3 .

It must be noted, however, that the values of $[CO^+]/[CN]$ cannot be ultimately considered as proportional to the $[CO]/[CN]$ relative abundance. The variability of the ionization mechanism due to the instability of the solar wind-comet interaction may cause variations in the CO^+ emission in a large range.

The estimated mean value for the relative abundance in Comet Humason of $[CO^+]/[CN] = 10^3$ should be assumed as a tentative minimum for $[CO]/[CN]$ in regard to an extreme stability of CO.

Generally, it appears that the variations of the relative abundances of molecules are very large among comets and depend on the composition of the cometary nucleus.

According to Rémy-Battiau and Swings [12] some comets with relatively strong continuum and faint or absent Swan bands seem to exist also among periodical comet families, for instance P/Comet Pons-Winnecke. On the contrary for P/Comet Faye at heliocentric distance $r = 1.7$ the $C_2(\Delta v + 1)$ was more intense than $CN(\Delta v = 0)$, which was a very unusual appearance for cometary spectra at large heliocentric distances.

3. Interstellar Abundance

a) H I region

The abundances of diatomic molecules have recently been determined for H I regions (Solomon and Klemperer [13]) by assuming gas-phase chemical reactions in the interstellar gas with the cosmical elemental composition. The abundances of diatomic molecules composed of H, C, N and O were determined as functions of hydrogen density, kinetic temperature and optical depth for the UV radiation significant for photodecomposition and ionization. The relative molecular abundances following from the Solomon and Klemperer [13] results are shown in Table 2 for $[CN]/[CO]$ for a somewhat denser model than the moderate one.

Table 2. Fractional Molecular Abundance $[CN]/[CO] \times 10^2$ for H I region $H = 10^3 \text{ cm}^{-3}$

$T_{kin} \text{ K}$ $\tau_{1000 \text{ \AA}}$	10	20	50	100
0	3.0	3.1	3.2	3.3
2	2.1	2.1	1.9	1.8
4	1.2	1.2	1.2	1.2
6	1.0	1.1	1.0	0.8

The mean values of $[CN]/[CO]$ are about 2×10^{-2} . The abundances $[H]/[CO]$ increasing in the same range of T_{kin} and from 4×10^{-9} up to 2×10^{-5} are due to the sensitivity of CO to the photodissociation in the radiation field below 1000 \AA , which is the only mechanism which can destroy this highly stable molecule in interstellar space.

According to [13] CO and CN are both produced primarily by a reaction involving CN and CH^+ , while the radiative associations as $C^+ + O^+ = CO^+ + h\nu$ or $C^+ + N = CN^+ + h\nu$ may be neglected. Therefore the dissociation of CH and CH^+ leads to more stable molecules and species of CH type may exhibit some decrement in the dense clouds.

The computed interstellar abundances of $[CN]/[CO]$ are higher [14], [15] than those observed in the optical and ultraviolet regions and 10^3 times higher than follows from the microwave results [16] where $[CN]/[CO] = 10^{-5}$. However, the optical data are uncertain and radio observations provide information for dense clouds with a high τ , where theoretical results [13] are not applicable because of high abundance of H_2 .

The very recent measurements in the microwave region [17] lead to $[\text{CN}]/[\text{CO}] = 2.5 \times 10^{-2}$ for the low-density region. Nevertheless, a possible decreasing abundance of CN relative to that of CO in a dense cloud should be the most interesting behaviour in the molecular formation in regard to a hypothetical process in solar nebulae.

The destruction of CN occurs almost only by photodissociation. There exist two exothermic reactions: $\text{CN} + \text{O} = \text{CO} + \text{N}$ and $\text{CN} + \text{N} = \text{C} + \text{N}_2$. However, the rate constant (in $\text{cm}^3 \text{sec}^{-1}$) for the first is $10^{-11} \exp(-1200/T)$ and for the latter 10^{-13} , respectively; therefore at low temperatures entirely ineffective or negligibly small. As Solomon and Klemperer have already stated, CN concentration increases approximately linearly with density and exponentially with optical depth. But the observations indicate that this process is evidently slowed down at a certain density, where either the binding of CN with other compounds or its destruction by exothermic reactions in locally thermalized regions governs the CN abundance.

The fractional abundance $[\text{C}_2]/[\text{CO}]$ obviously is very sensitive to the optical depth of the cloud, as follows from [13]: For $\tau_{1000\text{\AA}} = 0$, $[\text{C}_2]/[\text{CO}] = 0.4$; but if $\tau_{1000\text{\AA}} = 4$, then the ratio of C_2 to carbon monoxide will be about 10^{-2} and decrease to 10^{-3} for $\tau_{1000\text{\AA}} = 6$. Consequently the abundance $[\text{CN}]/[\text{C}_2]$ varies from 1 for a low τ to 10 in a highly opaque cloud.

For a moderate dense H I region with $\tau_{kin} \sim 50$ K the value of $[\text{CN}]/[\text{C}_2] = 5$.

b) Region with $T_{kin} > 1500$ K

The formation of some stable molecules occurs in stellar atmospheres and consequently in any medium in which thermochemical equilibrium may be established. Simplified calculation can be made for the partial pressure of atomic P_A , P_B and molecular constituents P_{AB} of a denser cloud using the well-known relation.

$$\frac{P_A P_B}{P_{AB}} = \frac{u_A u_B (2M)^{3/2}}{u_{AB} h^3} (kT)^{5/2} e^{-(D/RT)}$$

where D is the dissociation energy, u_{AB} the partition functions for given electronic, rotational and vibrational states of the molecules, and T the cloud temperature.

In a similar way Shimizu [18] obtained partial pressures for a model of a very dense cloud with an average cosmical abundance, assuming $P_h = 10^6 \text{ dyn cm}^{-2}$ and in the ranges of $T = 1500$ to 5000 K, i.e. for conditions resembling those for atmospheres of late-type stars.

The results for CN, C_2 and CO are shortly summarized in Table 3.

The relative abundances of CN to C_2 are lowest for $T = 5 \times 10^3$ K, where $[\text{CN}]/[\text{C}_2] \sim 10$ to 30 , and increase up to 10^4 in a cooler atmosphere (about $T = 4 \times 10^3$ K). The sensitivity of $[\text{CN}]/[\text{C}_2]$ to the temperature is so high that even a small temperature gradient in the nebula can lead to drastic variations in the relative abundance of these two diatomic molecules. Similar results follow for $[\text{CO}]/[\text{CN}]$ or $[\text{CO}]/[\text{C}_2]$. The concentration of the overabundant CO is 10^4 times higher than that

of CN for $T \sim 5 \times 10^3$ K and more than 10^7 times for a cool nebula ($T \leq 3000$ K). H_2O abundances estimated for models of dense clouds are important results for the condensation process preceding comets' formation. The total number of H atoms in atmospheres of the recent bright comets was about 10^{36} (see [19], [20], [21]), which is in agreement with Biermann's prediction [22]. OH is probably the second most

Table 3. Relative Abundances of CN, C_2 , H_2O for Dense Nebulae*)

T K	[CN]/[C_2]	[CO]/[CN]	[H_2O]/[CN]
5000	1.5	3.3	0.8
4500	2.6	4.1	2.1
4250	3.8	4.4	3.2
4000	4.2	4.6	4.0

abundant molecule in the cometary atmosphere. If H_2O is the precursor of atomic hydrogen and hydroxyl, then it can be expected that H_2O outnumbers CN or related constituents by factor $> 10^3$. From the computation for the thermochemical equilibrium follows that for $T \sim 4000$ K the ratio $[\text{H}_2\text{O}]/[\text{CN}] = 10^3$ and $[\text{H}_2\text{O}]/[\text{C}_2] = 10^5$ can be expected.

For temperatures of about 5×10^3 K the abundances of H_2O decrease rapidly with increasing temperature and $[\text{H}_2\text{O}]/[\text{CN}]$ approaches 1. Therefore pure gaseous nebulae with lower temperatures exhibit a considerably higher concentration of H_2O than of CN only if $T \leq 4000$ K. Under this condition CN is highly overabundant in respect to C_2 .

c) Influence of Interstellar Grains

Equilibrium abundances for various molecules in H I regions were estimated by Watson and Salpeter [23] on the basis of their theory of molecular formation on grain surfaces, and rates for gas-phase reactions and photodissociation. The results depend again strongly on hydrogen density and optical depth. The authors introduced a parametr $\xi = (n/100 \text{ H}) e^{2.5\tau}$, where n is the gas density in cm^3 and τ the visual optical depth. For low and high dense clouds they estimated the following relative abundances: For $\xi \simeq 1$, the fractional densities relative to atomic hydrogen are $\text{CN} = 4 \times 10^{-8}$, $\text{H}_2\text{O} = 10^{-9}$, $\text{CO} = 4 \times 10^{-7}$. For $\xi = 10$, $[\text{CO}]/[\text{CN}] \sim 10^4$; $[\text{H}_2\text{CO}]/[\text{CN}] \sim 1$. For the relative abundance of $[\text{HCN}]/[\text{CN}]$ the predicted ratio 10 to 10^2 is appreciably smaller than the observed one and HCN is probably produced directly on the grains. Therefore, in high density clouds for which $\xi \geq 300$ (where the mechanism assumed by Watson and Salpeter became invalid) the depletion of CN by formation of HCN must be expected. Unfortunately, no estimation has been made for C_2 .

*) Expressed in $\log(P_1/P_2)$ where P_1 and P_2 are partial pressures.

4. Conclusions

The estimated relative abundances $[\text{CN}]/[\text{C}_2]$ for interstellar conditions resemble the observed values for abundances of these two diatomic molecules in cometary atmospheres only if models of gaseous clouds with a low density and $T \sim 50$ K are taken into consideration. For a heated dense cloud the relative abundances of CN, C_2 and other molecules, which are in the frame of interest for cometary formation, are in serious disagreement with the observed abundances.

If a cometary nucleus preserves free radicals created in prestellar nebulae, then we must conclude that the calculated rates concerning the formation of molecules based on the assumption of the gas-phase reaction leads to unrealistic results for dense clouds.

The role of dust grains must be considered as a dominant mechanism in such an environment, which does not seem to be surprising in regard to the interstellar grains concentration.

The cometary relative abundance of CN in respect to C_2 may be underestimated. Moreover, the observed values represent only an instant situation in a relative short time interval of observation and the results cannot be used for determining some average value of $[\text{CN}]/[\text{C}_2]$. Nevertheless, the problem of a relative low concentration of CN remains in view of the possible growth of this radical with increasing density of a pure gaseous cloud. The situation becomes very paradoxical because C_2 can undergo fast exchange reactions and may be transformed into CN or CO. Therefore $[\text{CN}] \gg [\text{C}_2]$ can be expected even if the absolute values for both molecules in a very dense cloud are somewhat smaller because free C is considerably depleted by the CO formation. Generally we can expect that $[\text{CN}]/[\text{C}_2]$ in cometary atmospheres should be considerably greater than 1, which contradicts the observations and it seems to be very unlikely that even improved measurements would lead to quite different results. This fact implies that the originally relatively high abundance of the free CN radical decreased due to the binding in such interstellar molecules as $\text{CH} \equiv \text{C} - \text{C} \equiv \text{N}$; $\text{H} - \text{C} \equiv \text{N}$; $\text{H} - \text{N} \equiv \text{C}$, or other more complex molecules as HCNO. The reaction of CN with H producing HCN on interstellar grain surfaces may be very effective.

Moreover, the presence of dust is necessary for an effective condensation of H_2O in the further process of the "cometesimals" formation.

No firm answer can be given whether free radicals really are preserved in the cosmical ice lattice in the form of gas hydrates (i.e. clathrate hydrates) and whether the observed radicals are products of the fragmentation of large icy grains. But the decrement of CN in comets indicates that compounds as C_3NH ; HCN or HCNO must be present in cometary nuclei.

A more accurate determination of the molecular abundance in cometary atmospheres and of the variability of their relative concentrations would be one of the most important sources of information on the condensation process in the solar nebula.

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